

UNIV. OF
TORONTO
LIBRARY



Digitized by the Internet Archive
in 2008 with funding from
Microsoft Corporation

THE CHEMICAL NEWS, JANUARY 29, 1915.

THE
CHEMICAL NEWS

AND
JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

5.00
A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

VOLUME CX.—1914.

136138
614/15-

LONDON:

PUBLISHED AT THE OFFICE, 16, NEWCASTLE STREET, FARRINGDON ST.,
E.C.

AND SOLD BY ALL BOOKSELLERS.

MDCCCXIV.

LONDON:
PRINTED BY EDWIN JOHN DAVEY,
16, NEWCASTLE STREET, FARRINGDON STREET,
E.C.

THE CHEMICAL NEWS.

VOLUME CX.

EDITED BY SIR WILLIAM CROOKES, O.M., D.Sc., Pres.R.S., &c.

No. 2849.—JULY 3, 1914.

CONSTITUTION OF THE BENZENE NUCLEUS WITH REFERENCE TO THE PHENOMENON OF DI-SUBSTITUTION.

By BERNHARD FLÜRSCHHEIM.

UNDER the above title Mr. Cecil L. Horton recently (CHEM. NEWS, 1914, cix., 157) published certain theoretical views. In discussing these it is only necessary to deal with the last eight lines; for—although Mr. Horton appears to have overlooked the fact—everything else in his article had previously appeared in publications by the present writer (*Fourn. Prakt. Chem.*, 1902, lxvi., 321; 1905, lxxi., 497; 1907, lxxvi., 165, 185; *Ber.*, 1906, xxxix., 2015; *Fourn. Chem. Soc. Trans.*, 1909, xcv., 718; 1910, xcvi., 84), and can now already be found in some textbooks and other publications (for instance, Hans Meyer, "Analyse und Konstitutionsermittlung Organischer Verbindungen"; Richard Meyer, *Fahr. der Chemie*; "Annual Reports on the Progress of Chemistry," 1909, vi., 61, &c.).

According to the present writer's theory, an unsaturated atom in direct combination with the benzene nucleus causes an increase of free affinity in the ortho- and para-positions with regard to itself, and therefore substitution in these positions. In applying this principle to carbonyl and similar groups, Mr. Horton, in the last eight lines of his article, finds it necessary to make a supplementary assumption:—Since these radicles are unsaturated and still do not mainly direct into the ortho- and para-positions, it is, in his opinion, necessary to assume that such groups are first transformed by addition of the reagent, whereupon the latter migrates into the meta position.

If it were necessary to have recourse to additional hypotheses of this nature, the whole theory would have no value whatever. There would obviously be no reason why some other groups, for instance, methoxyl, should not also first add, say, nitric acid, and then be substituted in the meta-position. We should not have a comprehensive generalisation permitting to *foresee* anything, but simply a series of "explanations" *ad hoc*.

Mr. Horton's assumption is, however, wholly unnecessary. If a carbonyl or similar group is unsaturated, it does not follow that the particular atom by which it is linked to the nucleus is also unsaturated. It would be so according to Thiele's theory of partial valencies; but it would not be so according to the views advanced by Werner ("Beiträge zur Theorie der Affinität und Valenz," Zürich, 1891) in connection with the carbonyl-group in aliphatic acids. Werner argued that this group is linked to the neighbouring carbon atom with an abnormally low amount of affinity, because the bulk of the carbonyl-carbon atom's affinity is saturated by oxygen. On this idea of

Werner the present writer has based the following generalisation:—When an unsaturated atom (trivalent nitrogen, bivalent oxygen, monovalent halogen, &c.) takes the place of hydrogen linked to carbon, the demand thereby made on the affinity of the carbon atom is increased (not reduced) in amount. That substitution of methyl-hydrogen in toluene by unsaturated atoms must gradually lead to inversion of orientation is a postulate of this theory, and does not require any special hypothesis.

Which of these two diametrically opposed views on carbonyl and similar bonds is correct may be deduced from independent evidence. If, for instance, C in $-\text{CO}$ were, in accordance with Thiele, more unsaturated than C in $-\text{CH}_2$, carbon monoxide might be expected to have a greater tendency to polymerisation than methylene; the other view leads to foresee the opposite, and this, of course, corresponds to fact.

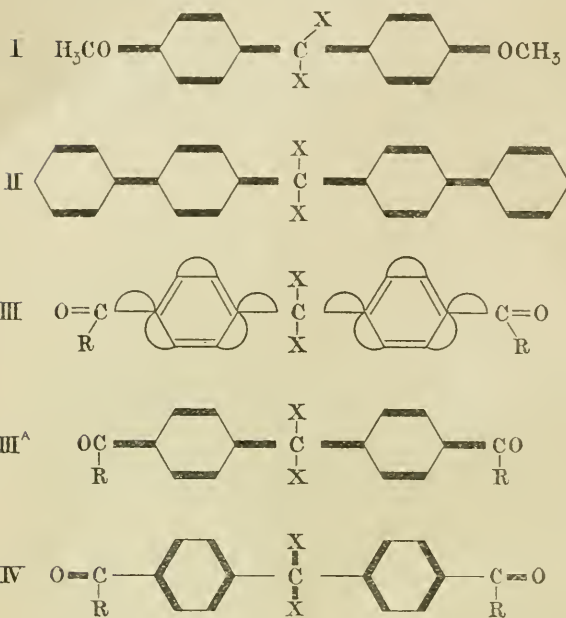
Again, if C in $-\text{CO}$ were unsaturated, the effect which the latter radicle would have on the mobility of certain atoms in side-chains would lie in the same direction as the action of other radicles with admittedly unsaturated atoms in corresponding positions. Thus a phenyl- or methoxyl-group in the ortho- or para-position is known to increase

the mobility of x in compounds of the type $\text{C}_6\text{H}_5\cdot\text{C} \begin{array}{l} \diagup \\ \diagdown \end{array} x$

(x = halogen, hydroxyl, &c.). According to the view first advanced by the present writer, and now accepted by most authors, this is due to a shifting of the distribution of affinity in the molecule, caused by the increased amount of benzene-carbon affinity taken up by the unsaturated substituting atom, and resulting in a decrease of the affinity available for linking x . It can be expressed graphically by Formulæ I. and II., the thick lines representing increased, and the thin lines decreased, amounts of affinity. If these substituents are replaced by carbonyl-radicles, Formula III. (or III.a which has the same meaning) would result according to Thiele's theory, IV. according to the writer's; by the former theory the mobility of x would be greater than in the unsubstituted compound, by the latter theory it would be less. As a matter of fact, Staudinger, Clar, and Zeako (*Ber.*, 1911, xlv., 1640), and Staudinger and Clar (*Ber.*, 1911, xlv., 1632) have found that the mobility is less.

Steric conditions cannot be made to account for these results, since they are practically the same in IV. as in I. Neither can the electro-negative nature of the carbonyl-group be adduced, since this would even tend to increase the mobility of x , according to universal experience concerning the mutual influence of electro-negative groups on each other. Neither can the "explanation" given by Staudinger—an adherent of the Thiele theory—that OCH_3

is an auxochrome, $\begin{array}{c} \text{CO} \\ | \\ \text{R} \end{array}$ a chromophore; these are merely words, quite apart from the fact that phenyl, which acts like methoxyl, is *not* an auxochrome.



R = Cl or OCH₃

The reactions of "conjugated double bonds" had not lent themselves to an experimental decision between the two theories. The reduction of ketones to pinacones had, even on the basis of the Thiele theory, necessitated the assumption that it was the oxygen which reacted first. But if these reactions had not given any indication of free affinity at the carbon atom of a carbonyl-group, they also had not disproved it. It is in the aromatic series that a crucial test has now been possible, and the verdict is against an unsaturated carbonyl-carbon atom as postulated by Thiele's theory of partial valencies, and therefore against that theory itself.

GAS ANALYSES BY FRACTIONAL DISTILLATION AT LOW TEMPERATURES.*

By G. A. BURRELL and F. M. SEIBERT.

THIS paper describes experiments that resulted in the separation of a natural-gas sample into the individual paraffin hydrocarbons present. This had not been accomplished hitherto.

Natural gases may contain only methane as the combustible constituent or may be mixtures that contain large quantities of the higher gaseous paraffins. In some samples the latter predominate. In addition, there may be vapours of the liquid paraffin hydrocarbons present, sometimes enough to warrant the installation of a plant for their extraction. The natural gas used in Pittsburgh, Pa., is a complex mixture, and is typical of gas that is supplied to many cities to the extent of billions of cubic feet per year. The exact composition of this gas is of importance to the

Bureau of Mines, because it is used in testing explosives, safety lamps, electrical mining machinery, and other mining appliances. By the scheme shown herein it is also possible to determine more closely the quantity of the vapours of the liquid paraffins in a natural gas mixture than has been possible heretofore. Gases that contain enough of these vapours are compressed and cooled at many plants and the condensate sold as gasoline.

It is generally known that ordinary combustion gas analyses give but little indication regarding the individual hydrocarbons present in a natural gas mixture. Only the two predominating paraffins are shown.

In the experiments reported herein, natural gas was first liquefied by means of liquid air, and the different paraffin hydrocarbons separated by properly adjusting temperatures and removing the various fractions with a mercury pump. These fractions were analysed by the ordinary slow combustion methods. Advantage was taken of the work of P. Lebeau and A. Damiens (*Comptes Rendus*, 1913, clvi., 325), who prepared various mixtures of the gaseous paraffins, liquefied them, and partially separated them. This work is an advance over their work in that the separation was made into single constituents. The important part of this paper, however, is the application of the work to the determination of the constituents of natural gas. Such a separation is possible because in the liquid condition the boiling-points of the gaseous paraffins are rather widely separated. These boiling-points follow:—Methane, -160° C.; ethane, -93° C.; propane, -45° C.; N-butane, +1° C., and isobutane -10° C. The two butanes were not separated. In order to finish the work with fractions large enough for accurate analyses the experiment given herein was started with about 1½ litres of gas (1531 cc.). Other experiments were performed with various natural gases in which smaller quantities were used. The sample as analysed by ordinary slow combustion methods contained the following constituents:—

	Per cent.
Methane	79.2
Ethane	19.6
Nitrogen	1.2
	100.0

There is also about 0.03 per cent of carbon dioxide in the gas mixture. Carbon monoxide, hydrogen, and olefine hydrocarbons are not present.

The experimental procedure follows:—

Fig. 1 shows the general arrangement of the apparatus. The Topley pump is on the left of the photograph. (A) is a small glass vessel used for holding the liquefied gases. It could be enclosed in the Dewar flask (B). Surrounding this Dewar flask is shown another and larger one. This arrangement was adopted in order to provide better insulation than was afforded by only one flask. The gas sample prior to liquefaction was measured in the glass vessel (c), then transferred to the gas burette (d), and from there passed into the liquefying bulb (A). At (E) is shown a mercury manometer for registering pressures in the pump. At the base of the Topley pump are shown the glass vessels for trapping the different gas fractions over mercury as they were removed.

The entire sample was first liquefied by means of liquid air or liquid oxygen. With the gas in the liquid condition, connection was made between it and the mercury pump, and as much of the gas removed with the pump as possible. This process divided the original quantity into two portions; first, a gaseous portion; and second, a liquid residue.

In other words, the vapour pressure of liquid ethane (boiling-point -93° C.) is so small at the temperature of liquid air that none could be detected in the distillate within the experimental error of making the analysis. It was found that when liquid air was used that had stood for some time so that its boiling-point had risen to a point

* Paper presented before the Spring Meeting of the American Chemical Society, April 7-10, 1914, by permission of the Director of the Bureau of Mines, U.S.A.

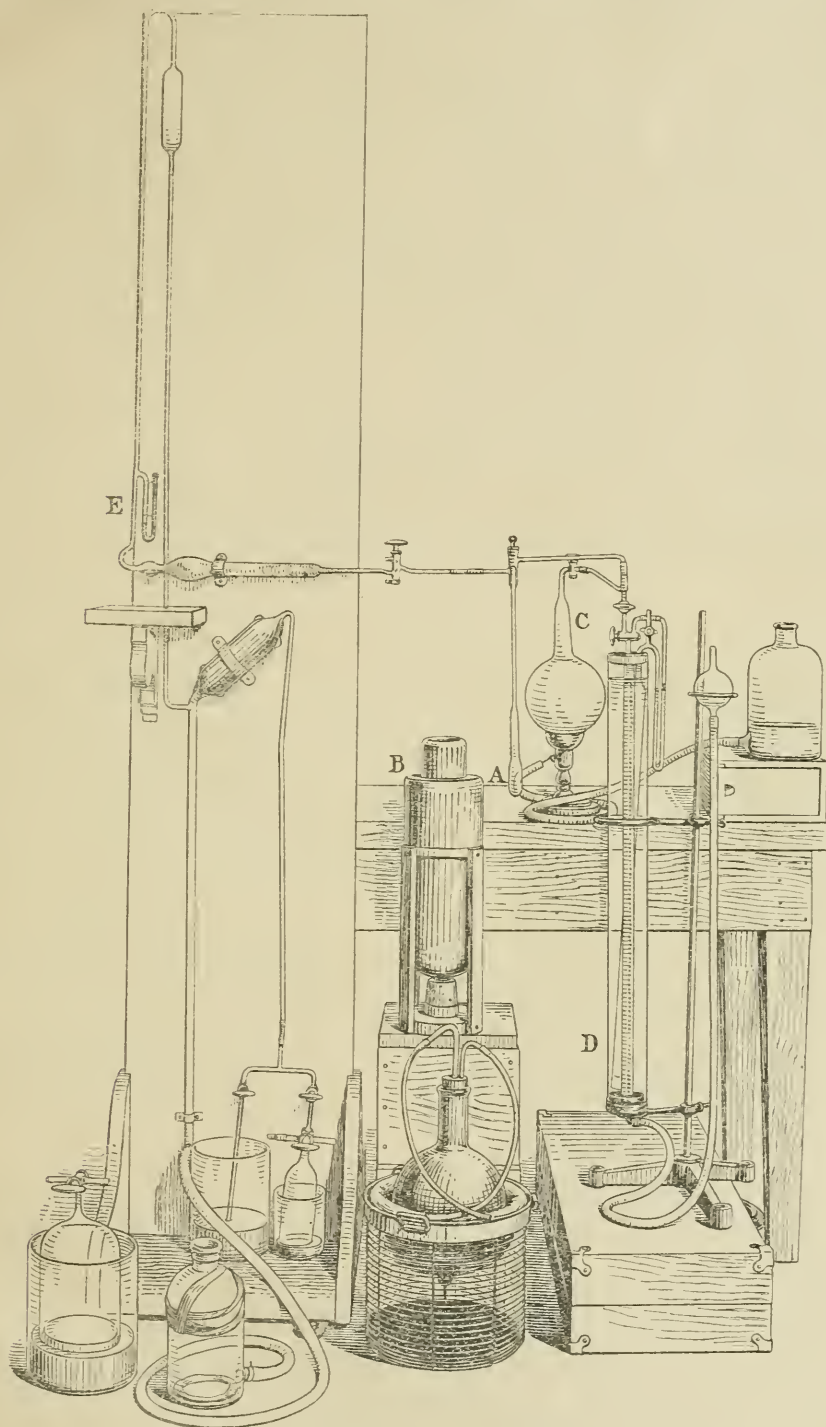


FIG. 1.—APPARATUS FOR FRACTIONAL DISTILLATION OF GASES AT LOW TEMPERATURES.

near to the boiling-point of oxygen ($-183^{\circ}\text{C}.$), that the methane and nitrogen were removed from the original mixture more quickly than when newly made liquid air was used. This is to be expected. The residue from this first

fractionation was allowed to volatilise, measured, and again liquefied at the temperature of liquid air. Connection was again made to the pump, and more methane removed. In other words, although the residue from the

first fraction was treated in exactly the same manner as the original sample more methane was obtained.

Upon volatilising the entire residue, however, and again liquefying a re-arrangement of the solution occurred, and chance for faster evaporation of this last methane portion was afforded. In no case could the last minute portions be recovered, so the attempts at complete recovery were stopped when it was found that only such a small proportion was being left behind as did not sensibly affect the results.

To this point the first series of fractionations had reached a stage where the larger portion of the methane had been removed by the first fractionation and where the first residue had been volatilised, re-liquefied, and pumped to obtain another small portion of methane. The residue from the second liquefaction was treated again in the same identical manner, and more methane obtained. A further identical treatment resulted in no additional recovery of methane. No indication of methane was found in the ethane portion within the error of making the analysis.

The distillate obtained by the above scheme undoubtedly contained a trace of ethane, but so small that it could not be detected by analysis. The analysis of a portion of the total methane and nitrogen fraction follows:—

TABLE I.—Analysis of a Portion of the Total Methane and Nitrogen Fraction.

	Cc.	Cc.
Sample taken	30.10	30.20
O ₂ added	95.20	99.30
Total volume	125.30	129.50
Volume after combustion	66.30	70.10
Contraction due to combustion ..	59.00	59.40
Volume after CO ₂ absorption ..	36.80	40.50
CO ₂ produced by combustion ..	29.50	29.60
(a) Methane from contraction ..	29.44	29.64
(a) Methane from CO ₂	29.59	29.67
Per cent methane from contraction	97.8	98.2
Per cent methane from CO ₂ ..	98.3	98.2
Average per cent methane	98.1	98.2

(a) Corrected for the molecular volume of CO₂.

Second Series of Fractionations.

The next step in the process involved the separation of the ethane from the methane free residue. This necessitated the employment of a temperature such that practically all of the ethane could be separated from the still higher paraffins, propane, the butane, &c. The temperature used could not be too low, else the ethane itself could not be separated, nor so high as to also remove all the propane. A natural gas condensate obtained from a natural gas gasoline plant by subjecting natural gas (casing head gas) from an oil well to a pressure of 250 lbs. per square inch, and then cooling it to ordinary temperature, proved excellent when cooled by liquid air for obtaining temperatures higher than the temperature of liquid air. This condensate is known in the natural gas gasoline trade as "wild" gasoline. It contains large quantities of liquid propane and the butanes (especially the latter), as well as some of the ordinary gasoline constituents, the pentanes, hexanes, &c. Other substances tried for obtaining low temperatures, such as alcohol, ether, methyl, and ethyl chloride, &c., jellied so much at low temperatures that they could not be used satisfactorily. The mass did not remain of uniform temperature from top to bottom.

In order to obtain a temperature of -145°C. , for instance, the condensate was placed in a Dewar flask and stirred with a test-tube into which liquid air was run until -145°C. was reached. Upon removal of the liquid air the condensate warmed up very slowly, about 5° to 10°C. per hour, thereby affording sufficient time for the withdrawal of the vapour from the liquefaction bulb. In separating ethane from the methane free residue the latter was first

cooled to a temperature of -145°C. , and pumping started and continued until the temperature had risen to -125°C. By this process there was obtained a distillate consisting of ethane and propane. In other words, some propane (boiling-point -45°C.) is removed at -125°C. as well as the ethane (boiling-point -93°C.). The residue was then treated twice in the same manner, the final separation of the ethane being made at a temperature of -155° to -140°C. The temperature was purposely lowered to -125°C. to obtain practically all of the ethane as well as some propane, because it was found easier to separate the ethane from that part of the propane that came over than to attempt to pull off all of the ethane from the original residue. All the ethane was obtained, there being only small quantities of propane remaining as a residue. The analysis of a portion of the total ethane fraction follows:—

Analysis of a Portion of the Total Ethane Fraction.

	1 (cc.).	2 (cc.).
Sample taken	25.50	20.30
O ₂ added	96.60	99.40
Total volume	122.10	119.70
Volume after combustion	58.30	69.20
Contraction due to combustion ..	63.80	50.50
Volume after CO ₂ absorption ..	7.20	28.70
CO ₂ produced from combustion ..	51.10	40.50

According to the equation $\text{C}_2\text{H}_6 + 3.5\text{O}_2 = 2\text{CO}_2 + 3\text{H}_2\text{O}$, the contraction should be equal to the $\text{CO}_2 \times 1.25$. In No. 1 analysis the contraction then becomes $51.1 \text{ cc.} \times 1.25 = 63.87 \text{ cc.}$ This corresponds well with the contraction actually observed, 63.80 cc. In No. 2 analysis the contraction is equal to $40.50 \text{ cc.} \times 1.25 = 50.62$. The contraction actually observed is 50.50 cc. In calculating the ethane from the carbon dioxide and contraction use was made of equations that correct for the deviations of carbon dioxide and ethane from the ideal conditions as follows ("Errors in Gas Analysis Due to Assuming that the Molecular Volumes of all Gases are Alike," by G. A. Burrell and F. M. Seibert, Technical Paper 54, U.S. Bureau of Mines; CHEM. NEWS, cix., 188, 196):—

No. 1 Analyses.

$0.990 \text{ C}_2\text{H}_6 + 3.5\text{O}_2 = 1.992 \text{ CO}_2 + 3\text{H}_2\text{O}$.
cc. ethane = $0.396 \times \text{contraction} = 25.26$.
cc. ethane = $0.497 \times \text{CO}_2 = 25.39$.

No. 2 Analyses.

$0.990 \text{ C}_2\text{H}_6 + 3.5\text{O}_2 = 1.994 \text{ CO}_2 + 3\text{H}_2\text{O}$.
cc. ethane = $0.397 \times \text{contraction} = 20.05$.
cc. ethane = $0.496 \times \text{CO}_2 = 20.09$.

Third Series of Fractionations.

The final residue from the second series of fractionations then contained propane and higher paraffins.

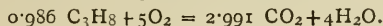
The ethane free residue was next liquefied and pumped at a temperature that started at -125°C. and ended at -110°C. , the object being to remove practically all of the propane (boiling-point -45°), and also some of the butanes (boiling-points $+1^{\circ}\text{C.}$ and -10°C.). The residue from this operation was again treated in the same manner to obtain any propane that still remained behind. It was thought that if a temperature was used that would permit the distillation of an appreciable quantity of butane, practically all of the propane should come over. The total distillate obtained in this manner was then liquefied, and pumped at a temperature ranging from -135°C. to -120° . There resulted a distillate that consisted of propane only. In other words, propane can be separated from the butanes at a temperature between -135° and -120°C.

The analysis of a portion of the total propane fraction follows:—

Analysis of a Portion of the Total Propane Fraction.

	No. 1 analysis.	No. 2 analysis.
	Cc.	Cc.
Sample taken	12'60	13'30
O ₂ added	93'80	97'20
Total volume	106'40	110'50
Volume after combustion.. ..	67'60	70'00
Contraction due to combustion	38'80	40'50
Volume after CO ₂ absorption ..	28'50	29'70
Carbon dioxide produced from combustion	39'10	40'30

According to the equation $C_3H_8 + 5O_2 = CO_2 + 4H_2O$, the contraction $-CO_2 = 0.0$. In No. 1 analysis 38.8 cc. -39.1 cc. $= -0.3$ cc., and in No. 2 analysis 38.1 cc. -37.9 cc. $= 0.2$ cc. The propane was calculated from the following corrected equation:—



Then according to No. 1 analysis the propane when calculated from the contraction is $0.329 \times 38.80 = 12.76$ cc., and when calculated from the CO_2 is $0.329 \times 39.10 = 12.86$ cc.

According to No. 2 analysis the propane when calculated from the contraction is $0.329 \times 40.5 = 13.32$ cc., and when calculated from the CO_2 is $0.329 \times 40.3 = 13.26$ cc.

In the case of both analyses the cc. of propane as calculated from the CO_2 and the contraction agree closely.

The value 0.986 or the molecular volume of propane at 0° C. and 760 mm. of mercury was calculated from Van der Waals' equation—

$$\left(P + \frac{a}{V^2}\right)(V+b) = RT$$

or—

$$\frac{M}{d_0}(1+a)(1-b) = R.$$

Cardoso gives for a the value 0.01727 and for b 0.003770, from which—

$$\frac{M}{d_0} = \frac{22.412}{1.0133} = 22.116$$

$$\frac{22.116}{22.412} = 0.986$$

This value, as far as the authors are aware, has never been verified experimentally as in the case of oxygen, methane, ethane, and carbon dioxide.

The same procedure was followed in the case of the propane separation as in the case of the ethane and methane separations. Distillates and residues were liquefied and pumped until no propane could be obtained.

The analysis of a portion of the final residue follows. This should consist of butane only, providing no vapours of the liquid paraffins are present.

Analysis of a Portion of the Total Butane Fraction.

	Cc.
Sample taken	9'30
O ₂ added	100'00
Total volume	109'30
Volume after combustion	76'30
Contraction due to combustion ..	33'00
Volume after CO ₂ absorption ..	39'30
CO ₂ produced by combustion ..	37'00

From the equation $C_4H_{10} + 5O_2 = 4CO_2 + 5H_2O$, the contraction $\times 1.14 = CO_2$. From the above analysis, $33.0 \times 1.14 = 37.62$ cc. $37.62 - 37.00 = 0.62$ cc. difference.

The above analysis was calculated to butane only, and appears to be almost entirely this gas, but undoubtedly a very small proportion of the vapours of the liquid paraffins were contained in the mixture.

Vapour pressures obtained by means of a manometer attached to the pump furnished evidence which indicated when a separation had been accomplished. For instance, at the temperature of liquid air the vapour pressure of the hydrocarbon mixture was 22 mm. This vapour pressure

was not the pressure of methane at that temperature, because some nitrogen was present. The pressure persisted throughout the pumping around this value until near the end, when it suddenly dropped to 0.0 mm. Then the pumping was stopped, and the residue allowed to volatilise, and again liquefied and pumping continued until no more distillate was obtained.

Three liquefactions of the residues were usually necessary for the removal of all the methane.

When the methane- and nitrogen-free residue was liquefied for the removal of the ethane the vapour pressure of the mixture was about 2 mm. at -155° , and about 4 mm. at -145° . When nearly all the ethane was removed, the pressure dropped off suddenly to 0.0 mm. when the pumping was stopped. The residue was again liquefied, and treated in the same manner until all the ethane was removed. Three successive treatments of the residue were usually sufficient.

After the removal of the nitrogen, methane, and ethane from the mixture had been accomplished, it became necessary to separate the propane from the butanes, &c. This was accomplished at -130° C. to -120° C. The vapour pressure at -130° C. was about 0.5 mm., and about 1 mm. at -125° C. The pressure dropped suddenly to 0.0 mm. after nearly all the propane had been removed. The residues were then treated as previously described until all the propane had been removed. The final residue consisted of the butanes and any vapours of the liquid hydrocarbons that were present.

(To be continued).

THE SEPARATION OF TITANIUM FROM IRON,
ALUMINIUM, AND PHOSPHORIC ACID
WITH THE AID OF THE AMMONIUM SALT OF
NITROSOPHENYLHYDROXYLAMINE
("CUPFERRON").

By WILLIAM M. THORNTON, Jun.

It has been shown by the author (*Am. Journ. Sci.*, 1914, xxxvii., 173) that titanium can be quantitatively precipitated in solutions moderately acidified with sulphuric acid and containing also tartaric acid by the ammonium salt of nitrosophenylhydroxylamine ("cupferron"). Making use of this fact, an indirect separation of titanium from iron has been accomplished. In this method, after precipitating the iron as ferrous sulphide by ammonium sulphide in the presence of ammonium tartrate and filtering from the aforesaid ferrous sulphide, the iron free filtrate is acidified with sulphuric acid, the hydrogen sulphide boiled out, and the titanium precipitated in the cold by the "cupferron" reagent. The yellow precipitate thus produced is collected and ignited to titanic oxide. At the close of the article it was stated that it would seem that there should be no great difficulty attending the separation of titanium from iron, aluminium, and phosphoric acid. Experiments with a view to accomplishing these separations have been fraught with very interesting and very gratifying results.

Although Schröder (*Zeit. Anorg. Chem.*, 1911, lxxii., 89) has made the statement that titanium and zirconium could be quantitatively precipitated by the "cupferron" reagent, no experimental data have appeared on the subject until Bellucci and Grassi (*Gazzetta Chimica Italiana*, 1913, xliii. [1.], 570) showed that titanium could be quantitatively thrown down by the reagent and that a clean separation of titanium from aluminium could be brought about by a single precipitation in acid solution. Their results leave little to be desired for accuracy. But it is indeed surprising that these writers do not give in any but the most indefinite terms the acid concentration or the absolute volume of the solutions in which the titanium was precipitated. They say that the solution should be

notably but not excessively acid with either sulphuric or hydrochloric acid. Again, under the separation of titanium from aluminium they say that the same acidity was used for the separation as for the precipitation of titanium alone, and that the precipitate was washed first by decantation and then on the filter with very dilute hydrochloric acid. Just how large a quantity of either of the above two acids can be employed and the precipitation of the titanium still be complete has not yet been determined. But the author's experiments have clearly demonstrated that if the concentration of sulphuric acid be too small, the aluminium is carried down with the titanium in considerable measure.

For these experiments two standard solutions of titanic sulphate were employed. These were made by acting on specially prepared potassium fluotitanate with concentrated sulphuric acid until all the hydrofluoric acid had been displaced, diluting and making up to known volume. The first solution was standardised by taking two weighed portions of 25 cc. each and precipitating the titanium by hydrolysis of the acetate upon boiling in the manner previously described by the author (*loc. cit.*, 174). Duplicate determinations gave the following results:—

Titanic sulphate solution.		Titanic oxide.	
(a) 25 cc. = 27.308 grms.	0.1427 grm.	0.5226 per cent	
(b) 25 cc. = 27.319 grms.	0.1428 grm.	0.5227 per cent	

Since these two results agreed so closely, the value obtained in (b) was arbitrarily taken as correct. The second solution was standardised by taking weighed portions of 25 cc. and 24 cc. respectively and determining the titanium in one (a) by the acetate method and in the other (b) by the "cupferron" method of Bellucci and Grassi (*loc. cit.*). Two determinations gave the following results:—

Titanic sulphate solution.		Titanic oxide.	
(a) 25 cc. = 27.814 grms.	0.1066 grm.	0.3822 per cent	
(b) 24 cc. = 26.667 grms.	0.1022 grm.	0.3822 per cent	

Since these two determinations agreed exactly, the value here obtained was taken as correct.

The first series of experiments were carried out with a view to obtaining favourable conditions for the separation of titanium from aluminium. Known quantities of aluminium were added by weighing off dry ammonium aluminium sulphate, which had been purified by two re-crystallisations. To the solution containing the titanium and aluminium and a weighed amount of tartaric acid (except in the case of experiments (1) and (2) which were made in the absence of tartaric acid), re-distilled ammonium hydroxide was added until the solution became neutral to litmus paper. A definite volume of sulphuric acid (made by diluting one volume of acid of sp. gr. = 1.84 with an equal volume of water) was then added and the solution made up to the volume designated in the last column of Table I. Twenty cc. of a 6 per cent "cupferron" solution was then added and the beaker set aside for the precipitate to settle. The time of standing does not appear to matter a great deal. Two hours was found to be satisfactory; but no doubt a shorter time would suffice, and in a few cases the precipitate was allowed to stand about twelve hours with no harmful consequences. The precipitate was filtered on paper with the aid of very gentle suction, washed twenty times with water containing 20 cc. of hydrochloric acid of sp. gr. = 1.20 per litre, placed in a tared platinum crucible, and dried at 110° C., ignited at first very carefully with the cover on, then with the crucible inclined, and open until all the carbon had been consumed, and finally brought to constant weight over the Meker burner. From experiments (1) and (2) it is evident that if the concentration of free sulphuric acid be too small, very serious errors are made in the direction of gain of weight on the titanium. Since, after the separation of the iron, the filtrate from the ferrous sulphide contains already tartaric acid, it was considered advisable at this point to earn the effect of tartaric acid on the next operation in

the analysis, viz., the separation of titanium from aluminium. Since the conditions in experiments (3) and (4) are the same as those in experiments (1) and (2) respectively, excepting the presence of tartaric acid, it is obvious that if this acid be present in the solution, the concentration of free sulphuric acid necessary to bring about a clean separation can be greatly diminished. In experiments (5) and (6) it will be noticed that with small increments in acidity the error is very slightly lowered. If the original solution for the analysis occupy a volume of 100 cc. the author has found that in his experience the filtrate and washings from the ferrous sulphide will occupy a volume of about 350 cc. An absolute volume of 400 cc. was therefore chosen as a convenient one in which to make the precipitation of titanium. Accordingly experiments (7) and (8) were performed with the object of learning the quantities of sulphuric acid and of tartaric acid necessary to effect a good separation in the above given absolute volume. In these two experiments the concentration of sulphuric acid was the same as in experiments (4) and the tartaric acid increased somewhat over the amount previously used. Since the results of experiments (7) and (8) were satisfactory it was not thought necessary to carry the series further.

TABLE I.—The Separation of Titanium from Aluminium.

No.	TiO ₂ taken. Grm.	Al ₂ O ₃ taken. Grm.	TiO ₂ found. Grm.	Error. Grm.	H ₂ SO ₄ (1:1) Cc.	Tar-taric acid. Grm.	Vol. of solution. Cc.
1.	0.1066	0.1127	0.1179	+0.0113	5	—	200
2.	0.1066	0.1127	0.1094	+0.0028	10	—	200
3.	0.05715	0.1127	0.0590	+0.0018	5	1.2	200
4.	0.0572	0.1127	0.0577	+0.0005	10	1.2	200
5.	0.0575	0.1127	0.0579	+0.0004	15	1.2	200
6.	0.0573	0.1127	0.0575	+0.0002	20	1.2	200
7.	0.1067	0.1127	0.1072	+0.0005	20	1.5	400
8.	0.1068	0.1127	0.1070	+0.0002	20	1.5	400

The second series of experiments was begun with the object of determining how great a concentration of sulphuric acid could be employed in the presence of tartaric acid without any resultant loss of titanium. The mode of procedure was the same as in the separation of titanium from aluminium except that in experiment (9) the precipitate was washed with water and in experiments (11) and (12) with hydrochloric acid (made by diluting 100 cc. of acid of sp. gr. = 1.20 to one litre). Since in experiment (12) the concentration of sulphuric acid was twice as great and the quantity of tartaric acid greater by half a gram, also than were found necessary to ensure a clean separation of titanium from aluminium, and since the error on titanium was one of gain, it appeared that there was little to be profited by carrying the series further.

TABLE II.

No.	TiO ₂ taken. Grm.	TiO ₂ found. Grm.	Error. Grm.	H ₂ SO ₄ (1:1) Cc.	Tar-taric acid. Grm.	Vol. of solution. Cc.
9.	0.1428	0.1429	+0.0001	5	0.5	200
10.	0.1066	0.1069	+0.0003	20	1.5	400
11.	0.1064	0.1067	+0.0003	30	2.0	400
12.	0.1064	0.1066	+0.0002	40	2.0	400

Fresenius (*Zeit. Anal. Chem.*, 1911, 1, 35) has succeeded in obtaining a quantitative separation of iron from phosphoric acid in a solution acid with hydrochloric acid by means of the "cupferron" reagent. Mindful of this, it occurred to the author that in a similar way it might be possible to separate titanium from phosphoric acid. The third series of experiments was therefore undertaken with this object in view. Approximately known quantities of phosphoric acid were added by weighing off dry portions of Baker's analysed disodium hydrogen phosphate. The conditions of experimentation were like those described above for the titanium aluminium separation. Table III.

TABLE IV.—The Separation of Titanium from Iron, Aluminium, and Phosphoric Acid.

No.	TiO ₂ taken. Grm.	Fe ₂ O ₃ taken. Grm.	Al ₂ O ₃ taken. Grm.	P ₂ O ₅ taken. Grm.	TiO ₂ found. Grm.	Error. Grm.	H ₂ SO ₄ (1:1). Cc.	Tartaric acid. Grm.	Volume of solution. Cc.
15.	0.1065	0.2036	0.1127	0.0154	0.1070	+0.0005	30	2	400
16.	0.1066	0.2036	0.1127	0.0151	0.1068	+0.0002	30	2	400
17.	0.1065	0.1018	0.1127	0.0153	0.1067	+0.0002	40	2	400
18.	0.1067	0.1018	0.1127	0.0153	0.1069	+0.0032	40	2	400
19.	0.1066	0.2267	0.2254	0.0153	0.1069	+0.0003	40	2.5	400
20.	0.1066	0.2267	0.2254	0.0153	0.1073	+0.0007	40	2.5	400

contains the results of two experiments. Since experiment (14) was entirely satisfactory, it was deemed unnecessary to extend the series further.

TABLE III.—The Separation of Titanium from Phosphoric Acid.

No.	TiO ₂ taken. Grm.	P ₂ O ₅ taken. Grm.	TiO ₂ found. Grm.	Error. Grm.	H ₂ SO ₄ (1:1). Cc.	Tar- taric solu- tion. Cc.	Vol. of solution. Cc.
13.	0.1064	0.0711	+0.1071	+0.0007	20	1.5	400
14.	0.1066	0.0710	+0.1067	+0.0001	25	1.5	400

It only remained to connect the three separations in order to complete the method of analysis. In experiments (15), (16), (17), and (18) known quantities of iron were introduced by adding weighed portions of Kahlbaum's ferrous ammonium sulphate. In experiments (19) and (20), a standard solution of ferric ammonium sulphate was used. In one portion (a) of 25 cc. the iron was determined by titration with potassium permanganate after reduction of the iron by zinc—the potassium permanganate having been previously standardised against sodium oxalate. In another portion (b) of 25 cc. the iron was determined by precipitation with ammonium hydroxide and ignition of the ferric hydroxide to ferric oxide. Parallel determinations gave the following results:—

Ferric sulphate solution.	Ferric oxide.
(a) 25 cc.	0.2267 grm.
(b) 25 cc.	0.2269 grm.

The value obtained in (a) was taken as correct. Throughout the fourth series of experiments a standardised solution of phosphoric acid was used. This was prepared by diluting Baker and Adamson's 85 per cent acid. In two portions of 25 cc. each the phosphoric acid was precipitated as ammonium magnesium phosphate. Duplicate determinations gave the following results:—

Phosphoric acid solution.	Phosphorus pentoxide.
(a) 25 cc.	0.15256 grm.
(b) 25 cc.	0.1528 grm.

The mean of these two values was taken as correct. Since the phosphoric acid present in titaniferous rocks is generally small in amount relative to the other constituents, it was thought best to dilute this dilution tenfold by volume. The resulting solution, therefore, contained in 25 cc. 0.0153 grm. of phosphorus pentoxide. In Table IV. are set forth the results of six experiments in which the whole analysis was performed.

For the benefit of the practical analyst the technique of the entire analysis is here connectedly given. To the solution, which should not be much greater than 100 cc. in bulk, at least four times the aggregate weight of the four oxides to be held by it in solution of tartaric acid is added. To facilitate the reduction of the iron the solution is made neutral with ammonium hydroxide and acid again with 2 cc. of sulphuric acid (1:1). Hydrogen sulphide is then introduced until the solution has become colourless. Unless the iron is thus reduced before precipitation, titanium will be in part thrown down also (A. Catherin, *Zeit. Kryst.*, 1882, vi., 243; 1883, vii., 250). Ammonium hydroxide is then added in decided excess and more hydrogen sulphide introduced until the iron has been com-

pletely thrown out as ferrous sulphide—leaving the solution, however, alkaline to test-paper. The ferrous sulphide is filtered off and washed with very dilute colourless ammonium sulphide about ten times. To the filtrate is then added 40 cc. of sulphuric acid (1:1) and the hydrogen sulphide thus liberated boiled out. After cooling to room temperature the solution is made up with water to 400 cc. and a 6 per cent solution of "cupferrom" added slowly with constant stirring. The beaker is then set aside for the precipitate to settle. After the precipitate has subsided the supernatant liquid is tested by adding a few drops of the reagent. The formation of a white precipitate of nitrosophenylhydroxylamine indicates that the reagent had been added in excess; whereas the formation of a yellow turbidity shows the precipitation to be incomplete. It is well also to test the filtrate. The precipitate is collected on a paper filter using gentle suction, and washed twenty times with hydrochloric acid (made by diluting 100 cc. of acid of sp. gr. = 1.20 to one litre). After having been sucked free of drainage water at the pump, the precipitate and filter are placed in a tared platinum crucible and dried at 110° C. (A quartz crucible is also satisfactory for the ignition). With the crucible not quite covered by the lid the ignition is begun with a very small flame. After the first violent gush of smoke the heat is raised a little, when the destructive distillation will proceed quietly. After burning away the carbon, the residual titanic oxide is brought to constant weight over the Meker burner. In the paper (*loc. cit.*) previous to this, where the separation of titanium and iron only was under consideration, the author has directed that the acidified filtrate from the ferrous sulphide be partially neutralised with ammonium hydroxide. It should be here noted that in the light of the further experiments recorded above, this is, of course, entirely unnecessary.

On account of the small amounts of platinum that find their way into the solutions during mineral and rock analysis, being derived from the platinum vessels by the attack of certain fluxes (such as alkali pyrosulphate or a mixture of sodium carbonate and potassium nitrate) on prolonged fusion or by the action of certain oxidising agents (such as sodium manganate, sodium chromate, &c.) on hydrochloric acid, and since Chatard (*Am. Chem. Journ.*, 1891, xiii., 109) in his modifications of the method of Gooch (*Proc. Am. Acad. Arts and Sci.*, 1885, xii., 435; see also Hillebrand, U.S. Geol. Survey, 1910, *Bull.* 422, 97, 107) has recommended the removal of platinum from the solution by hydrogen sulphide prior to the final precipitation of the titanium; it was thought advisable to find out whether or not the titanic derivative of nitrosophenylhydroxylamine carried down appreciable masses of platinum. Chlorplatinic acid was dissolved in water so as to make a solution containing approximately one mgrm. of platinum in every cc. Table V. contains the results of two experiments, which show that the precipitate has little, if any, tendency to include platinum.

TABLE V.—The Separation of Titanium from Platinum.

No.	TiO ₂ taken. Grm.	Pt taken (approx.) Grm.	TiO ₂ found. Grm.	Error. Grm.	H ₂ SO ₄ (1:1). Cc.	Vol. of solution. Cc.
21.	0.1067	0.0100	0.1071	+0.0004	40	400
22.	0.1067	0.0100	0.1066	-0.0001	40	400

The success of this analytical research has depended on three very fortunate phenomena. First: the precipitate of the titanium by the "cupferron" reagent is quantitative in the presence of tartaric acid—a fact which obviates the necessity of oxidising the tartaric acid. Second: the separation of titanium from aluminium is facilitated by tartaric acid to the extent of greatly diminishing the concentration of free mineral acid necessary. Third: a clean separation of titanium from phosphoric acid can be accomplished under the same conditions as the separation of titanium from aluminium, which seems to the author remarkable when one considers the insolubility of the basic phosphate of titanium even in decidedly acid media and the difficulties in handling these two substances in solution. The following points of merit are claimed for the method. The whole analysis is accomplished by two precipitations—the titanium being separated from both aluminium and phosphoric acid in one operation—so that the time required for the estimation of titanium in the presence of iron, aluminium, and phosphoric acid is no greater than the time required for the estimation of titanium when associated with iron only; since after filtering off the ferrous sulphide the technique is exactly the same in either case. The precipitate comes down immediately and quantitatively in the cold in flocculent and readily filterable condition, has little tendency to include alkalis, and after drying can be easily converted to titanate of a high degree of purity. The entire procedure is so simple that the attainment of good results by the analyst is almost inevitable.

In order that analytical chemists may have at hand directions for the preparation of the ammonium salt of nitrosophenylhydroxylamine an abstract of Baudisch's instructions for its synthesis is here appended (*Chem. Zeit.*, 1911, xxxv., 223).

Sixty grms. of nitrobenzene, 1000 cc. of water, and 30 grms. of ammonium chloride are stirred rapidly to an emulsion. Eighty grms. of zinc dust is added in small portions to the stirred emulsion by means of a knife blade; the temperature being kept between 16° and 18° C. by the occasional addition of a little shaved ice, until there is no longer an odour of nitrobenzene and the precipitate is grey. The reduction is accomplished in about one-half hour. The solution is filtered from the zinc hydroxide, which is washed a few times with iced water. The filtrate, cooled to nearly 0° C., is saturated with sodium chloride. Whereupon phenylhydroxylamine crystallises out in white needles. These are collected on a perforated funnel and dried by being pressed between filter-papers. The yield is generally 70–85 per cent of the theoretical. This body is a skin poison, and if spattered on the hands or face should be at once washed off with water and then with alcohol. The crystals are dissolved in 300–500 cc. of commercial ether, and the solution filtered from any residual sodium chloride. The ethereal solution, cooled to 0° C., is saturated with dry ammonia gas. While still at 0° C., the calculated weight of fresh amyl nitrite (1 molecule to every molecule of nitrobenzene) is added. The vessel is immediately filled with glistening white crystals of the ammonium salt of nitrosophenylhydroxylamine, $C_6H_5NO \cdot NONH_4$. After filtration and washing with ether, the crystals are dried by filter-paper, and kept in a closely stoppered bottle, in which is also placed a small lump of ammonium carbonate.—*American Journal of Science*, 1914, xxxvii., p. 407.

East London College (University of London).—At the meeting of the Council of the College held on June 22nd, it was announced that the Court of the Drapers' Company had resolved to defray the cost of the erection and equipment of the new chemical laboratories of the College. The cost will amount to approximately £15,000, and it is hoped that the laboratories will be available for the use of students at the commencement of the new session in October next.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

EVOLUTION OF THE SPIRILLÆ OF RECURRENT FEVER.

Dr. Roux, Director of the Pasteur Institute of Paris, has presented, before the Academy of Sciences, a paper by M. Nicolle, Director of the Pasteur Institute of Tunis, on the evolution of the spirillæ of recurrent fever in the bodies of lice. It is known that lice contaminated by the microbe of this affection are the active agents of the transmission of the disease. It is also known that a simple bite of these parasites is not sufficient to inoculate recurrent fever. The experiments made by M. Nicolle on monkeys have confirmed this fact, that in order to transmit the malady the lice must be crushed on an excoriation of the skin. This fact explains the relative frequency of recurrent fever in those populations to whom hygiene is unknown, as is the case with the natives of North Africa, whereas the disease is very rare in our countries.

CHEMICAL ANALYSIS BY SECONDARY RÖNTGEN RAYS.

Another paper read before the learned Assembly was one presented by M. Bouty and due to M. Broglie, describing the results of a new method of chemical analysis based on the employment of the secondary rays of the Röntgen radiations. M. de Broglie explains that the inspection of the secondary rays emitted by a compound submitted to the action of the X-rays enables one to recognise directly, in a very great number of cases, what are the composing elements, and that without it being necessary to make any manipulation on the substance that is to be tried. This method may have great advantages when precious objects are concerned or in certain cases of legal analysis.

SOME NEW EFFECTS OF THE ULTRA-VIOLET RAYS.

M. Jungfleisch presented a paper of Dr. Daniel Berthelot concerning the action of ultra-violet rays on oxalic acid. It results from this study that oxalic acid under the action of these radiations presents two different modes of decomposition, one at a moderate temperature the other at a high temperature, which has enabled M. Daniel Berthelot to form this conclusion, that the rapidity of vibration plays, in photo-chemical phenomena, a rôle analogous to that of the temperature of calorific phenomena. M. Dastre gave an account of an observation made by M. Sosonoff at the laboratory of physiology of Belgrade. By submitting, during a period of about twelve days, for about five or six hours a day, albino rabbits to the action of ultra-violet rays the fur of these rabbits becomes of a reddish yellow colour. The same modification of colour takes place in guinea-pigs, but in shorter time and with a less prolonged exposure.

ACCUSTOMING OF FERMENTS TO TOXICAL SUBSTANCES.

M. Charles Richet has placed a ferment in a lactic bouillon, into which he had introduced some toxics of which he increased the quantity every day. He remarked that the ferment became very quickly adapted to the nutritive toxic substance.

MARINE ANIMALS OF VERTICAL MIGRATIONS.

The Prince of Monaco gave some details before the Academy of Sciences on the strange marine animals of which he had spoken at the previous sitting, and which enjoy the property of displacing themselves twice a day on vertical distances of several kilometres without appearing to suffer in the least from the formidable depressions and re-compressions which result from these migrations. These animals have a very long tail, two strong mandibles, and their eye at the extremity of their upper jaw.

ATOMIC WEIGHT OF LEAD.

M. Moureu completed his preceding paper on the atomic weight of leads of different kinds by indicating that lead extracted from pitchblende has an atomic weight very decidedly inferior to that of ordinary galena lead.

A PREHISTORIC ANIMAL.

M. Deperet, Professor of the Faculty of Science of Lyons, presented the photographs of the reconstituted skeleton of a hitherto unknown prehistoric animal, the *Felsinotherium serresi*, that he has been able to reconstitute by the help of bones that he found in the five different layers of miocene of Montpellier. This animal, which is 2 m. 20 cm. long and 60 cm. wide, resembles the modern dugong and the present rhythine.

REGISTRATION OF TIME SIGNALS.

Up till now the only method of enregistering time radiotelegraphic signals was a photographic method. M. Jules Bailland, assistant astronomer at the Paris Observatory, has presented before the Academy a method of registration, not photographic, of the rhythmic time signals. The method consists in inscribing on a chronograph an auxiliary series of rhythmic signals that are rendered synchronous to the signals of the wireless telegraphy. Up till the present this auxiliary series was made by hand by the observer of the signals of the wireless telegraphy, and between the two series there may be a systematic difference of 0·1 second. In order to suppress this difference, M. Bailland produces the auxiliary series by means of a pendulum of the same period as the wireless telegraphy signals; according to a principle due to Lippmann, and which has already been applied by Guillet, he displaces the auxiliary series so that it coincides with the series of the wireless telegraphy. The signals coinciding with those of the wireless telegraphy are thus inscribed autographically on the chronograph.

MECHANISM OF THE INACTIVATION OF SERUMS.

In a new study presented before the Academy of Sciences by Prof. d'Arsonval, M. Tissot shows that the laws of the dissociation of soaps, which give the explanation of the mechanism of the inactivation of serums by heat and by dialysis, give likewise the explanation of the same phenomenon by the addition of precipitating salts, of diluted acids, carbonic acid, and globuline. The precipitating salts act in separating the globules bound to the acid soaps, and in determining correlatively a second alteration of the complement, characterised by an increase of the proportion of chloresterine directly extractable by ether. The inactivation by precipitation by means of carbonic acid or of strongly diluted acids is likewise to be explained in the same manner. The inactivation, by the addition of globuline, results from a modification of the soaps of the serum proceeding from the joining or association of the acid soap bound to the globuline with the more basic soap contained in the serum.

ALTERATION OF MEAT PRESERVED BY COLD.

Prof. Dastre presents to the Academy of Sciences a paper by M. Piettre, veterinary surgeon, attached to the sanitary inspection of the Central Market, on the putrefaction of meat, poultry, and game preserved by cold. From this paper it appears that any carcase freshly prepared is practically aseptic, but only meat the central parts of which are perfectly clean and unsoiled must be treated by cold. The putrefaction of meat relates to two distinct types: that of the surface produced at the contact of the air, by a fermentation of an ammoniacal and sulphhydic basis, and the putrefaction at a depth below the surface which, as a general rule, is not perceptible either from the smell nor from any special aspect. M. Piettre indicates that, in this latter case, a sure indication of microbial fermentation results from the presence, in the heart of the muscles, of crystallised tyrosine in white striated lines or in white masses; this substance is produced by the decomposition of the albumenoid matter. The presence of these white spots enables the meat that is thus attacked to putrefy.

EFFECTS OF FATIGUE ON BLOOD PRESSURE.

Does the pressure of the blood undergo the same modification under the influence of a purely physical fatigue as from that resulting from an intellectual work? Such is the question examined by M. J. M. Lahay in a paper likewise presented before the Academy by Prof. Dastre. The author has seen that the blood pressure does not increase in the first case, for which he has taken as an example soldiers who had accomplished a fatiguing march. In the second case, however, as in that of type-writers accomplishing a steady assiduous work, this pressure increases regularly. M. Lahay has already shown in former communications that the augmentation of the pressure of the blood and the greater duration of the time of reaction are the objective signs of fatigue in modern professions that require a fixed sustained attention. He now proves that these signs are "specific" of these professions.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 18, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

(1) "*Trypanosome Diseases of Domestic Animals in Nyasaland. Trypanosoma capræ (Kleine). Part III. Development in Glossina morsitans and Wild Game in the 'Fly-belt' of the Upper Shire Valley*;" (2) "*The Food of Glossina morsitans*;" (3) "*Infectivity of Glossina morsitans in Nyasaland during 1912 and 1913.*" By Surg.-Gen. Sir D. BRUCE, F.R.S., Maj. A. E. HAMERTON, Capt. D. P. WATSON, and Lady BRUCE.

"*A Description of the Skull and Skeleton of a Peculiarly Modified Rupicaprine Antelope, Myotragus balearicus (Bate).*" By C. W. ANDREWS, F.R.S.

"*Relation between the Thymus and the Generative Organs, and on the Influence of these Organs upon Growth.*" By E. T. HALNAN and F. H. A. MARSHALL. (With a Note by G. U. YULE).

"*Vapour-pressure Hypothesis of Contraction of Striated Muscle.*" By H. E. ROAF.

Two objections have been urged against muscular contraction being due to movements of water from one portion of the muscle fibre to another.

These are:—(1) That an osmotic model of muscle cannot cause a sufficient degree of shortening, and (2) that the movement of water would require a longer time than the muscle takes in contracting.

The extent of contraction possible for an osmotic model and the time required for this contraction has been calculated for structures of the dimensions of frog's sartorius. It is found that the extent of contraction can be explained by the osmotic model, and that the time required is less than 0·03", and frog's sartorius requires at least 0·04" for complete contraction.

So far as these two objections are concerned, differences of vapour-pressure can explain the phenomena of muscular contraction.

"*Validity of the Microchemical Test for the Oxygen Place in Tissues.*" By A. N. DRURY.

Experiments were made to show that the microchemical test with rongalit white, used by Unna to fix the position of the oxygen place in tissues, could be obtained on a surface entirely free from oxygen. A further extension of

the work showed that the condensation of a solute on to a surface is markedly influenced by the previous treatment of, or by the gas condensed on, that surface.

"*Man's Mechanical Efficiency.*" By J. S. MACDONALD.

The rate of heat-production, Q , associated with cycling at a uniform rate but with varied performances of mechanical work, is expressed in the following form:— $x + Ey = Q$, where x represents the heat production associated with a uniform rate of movement, y the rate of work-performance.

It is shown that E varies inversely with $W^{2/3}$. It follows that, putting on one side x , the energy-transformation entailed by the movements *per se*, the additional energy-transformation required for any definite rate of work-performance is less the greater the weight, W , of the worker, and the mechanical efficiency measured in this fashion varies directly with $W^{2/3}$.

It is also shown, however, that x varies approximately with $W^{3/2}$, and thus that the energy-transformation associated with the mere production of movement is much greater the greater the weight.

Experimenting with one subject, and thus with a constant value of W , but with variations in V , the rate of movement per minute, it is shown that, in this particular case, x has the value of $43V^{2/5}$. The interest in this special form of expression is that it assigns a maximum efficiency, per movement, to a certain intermediate rate of movement.

It is shown that a similar expression adequately covers published data of certain experiments in which the subject walked at different rates (Douglas and Haldane). The opinion is advanced that the nature of this expression is referable to the pendular character of the limb movements, and to the existence in each individual, and for each particular set of movements, of a certain natural rate.

"*Colouring Matters in the Compound Ascidian Diazona violacea (Savigny).*" By A. HOLT.

"*Some Accessory Factors in Plant Growth and Nutrition.*" By W. B. BOTTOMLEY.

Plant growth-stimulating substances are formed in sphagnum peat when it is incubated with a liquid culture of certain aerobic soil bacteria for a fortnight at 24°C .

These substances are soluble in water and in alcohol, and are active in very small amounts, two applications of water-extract of 0.18 grm. treated peat doubling the size of *Primula malacoides* seedlings over untreated plants in six weeks' time. They appear to be similar to so-called accessory food substances essential for nutrition of growing animals, first studied in connection with the deficiency diseases beri-beri and scurvy.

The production of these substances appears to be associated with formation of soluble humates in peat by bacterial action. They are not formed when peat is treated with alkalis. Cultures of *Azotobacter chroococcum* grown with extract of "bacterised" peat gave an increase of 18 mgrms. of nitrogen in eight days, whilst extract of chemically-treated peat gave no increased fixation.

The active substance is precipitated from aqueous solution of alcoholic extract of "bacterised" peat by phosphotungstic acid, and can be further separated by decomposing with baryta, re-precipitating with silver nitrate, and decomposing with hydrogen sulphide.

Wheat seedlings in sand culture with Detmer's complete food solution gave an increase of 22.7 per cent with the phosphotungstic fraction and 17.7 per cent with the silver fraction.

Water-culture experiments with wheat seedlings in Detmer's solution prepared from pure salts in physiologically pure distilled water showed that these substances are essential for assimilation of inorganic food constituents. In complete food solution the plants gained weight for a time, then lost weight and died; in complete food solution with the silver fraction extract added there was continuous growth and increase in weight. The weights of thirty seedlings taken every sixteen days were:—

Complete food:—

Weight in grms. . . .	4.73	5.42	5.29	4.33
Percentage gain or loss (per cent)	—	+14.7	+11.8	-8.4

Complete food + silver fraction:—

Weight in grms. . . .	4.73	5.57	6.65	7.33
Percentage gain or loss (per cent)	—	+17.7	+40.6	+54.9

These growth substances are also produced during germination of seed. Very young seedlings from which seeds were removed very soon died in pure culture solution; when supplied with silver fraction growth was normal.

Complete food:—

Weight in grms. . . .	3.20	3.37	3.20	2.85
Percentage gain or loss	—	+5.3	+0.0	-10.9

Complete food + silver fraction:—

Weight in grms. . . .	3.17	3.63	4.29	5.03
Percentage gain or loss	—	+14.5	+35.30	+59.30

"*A Photographic Analysis of Explosion-flames Traversing a Magnetic Field.*" By H. B. DIXON, C. CAMPBELL, and W. E. SLATER.

The authors have carried out a suggestion made by Sir J. J. Thomson that the explosion wave in gases should be photographed on a rapidly moving film while it traverses a strong magnetic field, to determine whether the emission of electrons in front of the wave "prepares the way" by ionising the gases. Using a very powerful magnet lent them by the kindness of Sir E. Rutherford, the authors have photographically analysed the explosion wave in different mixtures of gases before it enters, while traversing, and as it leaves, the magnetic field. In no case did the magnetic field alter the character or velocity of the flames.

NOTICES OF BOOKS.

Sanitary Engineering. By FRANCIS WOOD, M.Inst.C.E., F.G.S. Third Edition. London: Charles Griffin and Co., Ltd. 1914.

In the third edition of this book new matter dealing with the application of concrete in drainage work, the ventilation of sewers, &c., has been added, and the question of the disposal of flood water is treated somewhat more fully than before. The formulæ in hydraulics, &c., are carefully worked out from first principles, and a minimum of mathematical knowledge is required for understanding the processes employed. The book has been deservedly highly esteemed for the use of students, municipal engineers, and sanitary inspectors, and the third edition will serve the same useful purposes as the earlier issues.

The Sampling and Examination of Mine Gases and Natural Gas. The Inflammable Gases in Mine Air. By GEORGE A. BURRELL and FRANK M. SEIBERT. Washington: Government Printing Office. 1913.

In the first of these papers (*Bulletin* 42) details are given of the method of collecting samples of gases recommended by the Bureau of Mines, and special forms of gas analysing apparatus are described. These include apparatus which is suitable for accurate work as well as arrangements which can be employed when the chief desideratum is rapidity. The authors have also devised an apparatus which will give quite good results in the hands of totally inexperienced operators. The question of the constitution of the inflammable vapours in mines is one of the utmost importance, for if, for instance, ethane, hydrogen, ethylene, carbon monoxide, &c., are present, as has been

stated by some authorities, the ignition temperature will be lower than if methane only is present. In the second paper (Technical Paper 39) the authors describe the experiments they have made in studying this question. From the examination of 44 samples of gas from various mines they conclude that the only combustible gas present in normal mine-air is methane.

L'Industrie de l'Azote Atmosphérique. ("The Industry of Atmospheric Nitrogen"). By ALFRED TOBIANSKY D'ALTOFF. Paris: H. Dunod and E. Pinat. 1914.

THE importance of the problem of the discovery of sources of nitrogen in a form in which it can be directly assimilated by plants is admirably shown in this paper, which also discusses shortly the different methods of fixing atmospheric nitrogen which have been commercially successful. The processes included for description are treated in outline only, and the author writes more with a view to interest the general reader than to provide information for the expert. The economical aspects of the problem are not neglected, and the questions of cost and prices are considered.

Über die Analyse Radioaktiver Substanzen durch Sublimation. ("The Analysis of Radio-active Substances by Sublimation"). By CARL RAMSAUER. Heidelberg: Carl Winters Universitäts-buchhandlung. 1914.

No satisfactory and generally applicable method of quantitatively determining radium, thorium, and actinium present together in feebly active substances has been devised before, and hence the method suggested by the author for the purpose will be welcomed. Briefly the process depends upon the sublimation of the active precipitates accumulated in the substance upon a cooled surface; the decay curves are then ascertained and referred to the three fundamental curves of the pure substances. These three curves are calculated theoretically and experimentally verified. The experimental conditions are chosen so that the three curves show characteristic differences among themselves. The details of the method are described fully in the paper and applications of it in special cases are discussed.

Enzyklopädie der Technischen Chemie. ("Encyclopædia of Technical Chemistry"). Edited by Dr. FRITZ ULLMANN. Berlin and Vienna: Urban and Schwarzenberg. 1914.

THIS encyclopædia is to appear in ten volumes, which will be completed within three or four years. It is to include all the chemical industries, metallurgical processes and products, and also food stuffs, pharmaceutical preparations, drugs, &c. A special effort has been made to give a clear view of the present state of the various industries, and it has been found necessary to include some articles on purely scientific subjects. Comprehensive and lengthy articles form the ground-work of the encyclopædia; thus, under "Aniline" all the derivatives of aniline are included. The book is well indexed, subject indexes being provided for each part, as well as a general index for the whole.

Struttura Molecolare degli Atomi Radioattivi. ("Molecular Structure of Radio-active Atoms"). By G. ODDO. Rome: Tipografia Editrice Italia. 1914.

THE hypothesis put forward in this article is exceedingly ingenious, and deserves the careful study of all who are interested in the problems of radio-activity and the structure of the atoms of radio-active elements. The author suggests that this structure can be represented graphically by a single or double hexagon, like the benzene or naph-

thalene nuclei. Helium is regarded as taking the place of the hydrogen, and the transformation of one element into another is due to the loss of one or more helium atoms, while the loss of the imponderable electron gives rise to the rearrangement of the helium atoms, the resulting elements being comparable with stereo-isomers. The author has worked out the details of the transformations in the uranium, actinium, and thorium series, and gives a table showing all the supposed structural formulæ.

Anorganische Peroxyde und Persalze. ("Inorganic Peroxides and Persalts"). By Dr. C. FREIHERRN VON GIRSEWALD. Braunschweig: Friedr. Vieweg und Sohn. 1914. (2.40 M).

IN the last fifteen years the preparation of derivatives of hydrogen peroxide may be said to have taken its place as a new industry, and the working out of new and cheaper methods has proceeded with great rapidity. Electrolytically prepared persulphates are beginning to displace sodium peroxide as the technically most important source of active oxygen, and the statistics and data to be found in even modern text-books are becoming out of date. Hence this monograph, which contains descriptions of the most recent work and processes, will be a valuable addition to the library of the technical chemist. The first part of it deals with hydrogen peroxide itself, and discusses its constitution and technical preparation, and gives an account of the properties and strengths of the commercial preparations which have been placed on the market. In the second part dealing with the derivatives of hydrogen peroxide some allusions are made to those which are chiefly of theoretical interest, but the greater part of the text is devoted to the description of their preparation on a large scale and their practical uses.

Zur Lehre von den Zuständen der Materie. ("On the Theory of the States of Matter"). By Prof. Dr. P. P. VON WEIMARN. Vol. I. and II. Dresden and Leipzig: Theodor Steinkopff. 1914. (7 M).

THIS book is based upon a series of articles which appeared in the *Kolloid-Zeitschrift* in 1908 and 1909. Some necessary alterations and emendations have been made, and a good deal of the earlier part, which dealt more particularly with the theory of the colloidal, or as the author would call it the dispersoidal, state has been omitted. The photographs and illustrations have all been put together in Vol. II., and the two volumes form a very complete exposition of the author's well-known views on the problems of colloidal chemistry, and give a brief account of the experimental work upon which his opinions are based.

Jac. Berzelius Lettres. III. Correspondance entre Berzelius et Alexandre Marcet. ("Letters of Jac. Berzelius. III. Correspondence between Berzelius and Alexandre Marcet"). Upsala: Almqvist and Wiksells Boktryckeri, A.B. 1914.

THE letters which are contained in this book passed between Berzelius and the Swiss physician Alexandre Marcet between the years 1812 and 1822. Marcet was residing in England during the greater part of this time, and his letters give a vivid account of the scientific world of London; he was acquainted with most of the leading scientists of the day, and was himself a keen investigator and a man of great culture. The period, moreover, was one of great activity upon the part of Berzelius, and the letters contain discussions of prevalent theories and recently announced discoveries, while Berzelius's own researches are described; for instance, the preparation and investigation of selenium. A few explanatory notes are added to the letters which almost without exception have never been published before.

Kurzes Lehrbuch der Organischen Chemie. ("Short Text-book of Organic Chemistry"). By Prof. Dr. A. BERNTHSEN. Twelfth Edition, prepared in collaboration with Dr. AUGUST DARAPSKY. Braunschweig: Friedr. Vieweg und Sohn. 1914. (12 M).

PROF. BERNTHSEN has again had the assistance of Dr. A. Darapsky in preparing the twelfth edition of this book, which, appearing not much more than two years after the eleventh edition, has undergone very little alteration. The book has long been known as one of the best of its size on organic chemistry, and it has been kept in every respect thoroughly up-to-date. It is admirably suited for the use of beginners, both those who intend to specialise in pure chemistry and those who wish to enter upon a technical career, and abundant references are given to periodical literature and larger works, for the benefit of more advanced students.

Ricerche Sperimentali sui Raggi Magnetici in Diversi Gas e Miscugli Gassosi. ("Experimental Researches of the Magnetic Rays in Different Gases and Gaseous Mixtures"). By Prof. AUGUSTO RIGHI.

In this paper, read before the Reale Accademia delle Scienze at the meeting of November 16, 1913, the author described his new apparatus for studying the phenomena of the virtual anode, using discharging tubes of various forms. In these experiments measurements were taken of the distance between the virtual anode and the cathode, and tables and curves are given showing the values of the distance corresponding to different values of the magnetic field. The experiments were performed in air and in various other gases and mixtures of gases, and they tend to show that the author's doubts about the conclusions of More and Rieman about the virtual anode were well founded.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 19, May 11, 1914.

Synthesis by means of Sodamide. Action of Epialohydrines on Dialkylacetophenones, Oxypropylene-dimethylacetophenone, and Derivatives.—Mme. Ramart-Lucas and A. Haller.—The sodium dialkylacetophenones react on the epialohydrines to give compounds containing both the ketonic and the oxyethylenic functions. In these compounds it is the last function which usually enters into reactions. The oxypropylene-dimethylacetophenone prepared is very sensitive to the action of acids, and is readily transformed into a dimer, the melting-point of which, viz., 214° , differs by 155° from that of the original ketone oxide.

Researches on the Acid Salts of Dibasic Acids, Oxalates.—E. Jungfleisch and Ph. Landrieu.—The authors have studied the composition of the mother-liquors in which the different potassium oxalates have crystallised, producing a system in stable equilibrium. They have found that in liquors containing less and less neutral salt, and hence richer in water, acid potassium oxalate is decomposed by water into the neutral salt and free acid, the latter uniting with one part of the acid salt to give monopotassium dioxalate. If free acid and neutral salt are the products of the decomposition by water of the acid salt it may be concluded that the formation of the acid salt results from the union of one molecule of dibasic oxalic acid with one molecule of neutral potassium oxalate. The formation of acid oxalate corresponds, like the formation of acid salts of monobasic acids, to the combination of

free acid with neutral salt. Thus the acid oxalate would have the formula $\text{KCO}_2\text{CO}_2\text{K} \cdot \text{C}_2\text{H}_2\text{O}_4$, and not the formula usually adopted, $\text{HCO}_2\text{CO}_2\text{K}$.

Determination of the Atomic Weight of Nickel.—Æchsner de Coninck and M. Gérard.—A nitric acid solution of nickel was treated with H_2S , the iron was oxidised and precipitated with ammonia. The filtered liquid was treated with NH_4SH , the precipitate washed with hydrochloric acid, and then dissolved in aqua regia. The solution was evaporated to dryness, and the residue taken up with very dilute hydrochloric acid. The liquid was treated with BaCO_3 and a current of chlorine which separated the cobalt. The solution was filtered and precipitated with baryta, filtered, and again evaporated. The crystals were dissolved in water acidified with HCl , and precipitated with a concentrated solution of oxalic acid. The dihydrate, $\text{C}_2\text{O}_4\text{Ni} \cdot 2\text{H}_2\text{O}$, was decomposed by heating in a current of hydrogen and the metallic residue weighed. The mean value of the atomic weight thus obtained was $\text{Ni} = 58.57$.

Preparation of Normal Pentene.—M. Picon.—Normal pentene can be prepared from normal propyl iodide by the method previously described by the author for true acetylenic hydrocarbons. It is a sweet tasting mobile liquid with an ethereal odour. The difference between the boiling-points of the normal and homologous true acetylenic hydrocarbons is a fixed quantity, 31.5 to 32° .

Syntheses of Acetylenic γ -Diketones.—Georges Dupont.—Chromic oxidation in acetic solution converts the acetylenic γ -glycols obtained by Jotsitch's method into the acetylenic diketones. This method acts excellently with the aromatic but not with the fatty glycols. All the secondary glycols obtained by Jotsitch's method are mixtures of stereo-chemical isomers, but there is no need to separate the isomers, for on oxidation the asymmetry of the molecule disappears.

Catalytic Hydrogenation of Liquids at Moderate Temperature and Pressure.—André Brochet.—The hydrogenation of liquids under the influence of common metals, especially nickel, readily occurs at moderate temperatures and pressures, provided that the substances are well shaken to ensure frequent changes of the surfaces of contact. At the ordinary pressure compounds containing an aliphatic ethylenic bond are readily hydrogenated, but usually a pressure of some kilograms per square centimetre is necessary. The best results are obtained by judiciously raising the temperature and pressure. The method can be applied to the hydrogenation of compounds with acetylenic or ethylenic bonds, and also to the reduction of nitro-compounds, &c.

MISCELLANEOUS.

Notice of Removal.—Messrs. Frederick Jackson and Co., Ltd., announce that, in consequence of the premises they have occupied for the last thirty years being required for extension of the Royal Exchange, they have removed from 14, Cross Street, Manchester, to other premises situated at 44, Chapel Street, Salford, Manchester (near Exchange Station).

Relations between the Constitution and Thermic Properties of Binary Mixtures.—Paul Pascal.—Two symmetrical molecules of the type $\text{R}-\alpha-\beta-\gamma-\delta-\text{R}'$ always give a continuous series of mixed crystals, except when the aromatic nuclei are not all identical. When the fatty chain is asymmetrical and does not possess the same bonds and the same groups of atoms in the two constituents isomorphism gives place to dimorphism. Between these two extreme cases there are some cases of isomorphism when the identity and symmetry of the nuclear structure compensate for little isolated asymmetries in the central fatty chain.—*Bull. Soc. Chim. de France*, xv., xvi., No. 10.

THE CHEMICAL NEWS

VOL. CX., No. 2850.

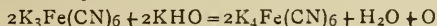
ESTIMATION OF ORGANIC MATTER IN WATER.

By PERCY KAY, Ph.D.

THE method of Förchhammer in its original and modified present form, viz., Tidy's modification, has always appeared to me unsatisfactory, as the oxygen absorbed is invariably much below the quantity actually needed to oxidise the organic matter. In view of this fact I devised a method, which though not new in principle, is so far as I am aware in application. It resembles the procedure adopted by Wanklyn in his Moist Combustion Method. The *modus operandi* is as follows:—About 500 cc. of the water is mixed with 1·1 or 1/3000th of the equivalent of potassium ferricyanide (molecular weight 329) together with about 3·5 cc. (1 fluid drachm) of strong caustic potash (1·27) or the strength employed in elementary organic analyses.

The whole is heated to boiling for about one hour. After cooling the excess of $K_3Fe(CN)_6$ is given by the addition of HCl a decided acid reaction; about 1 grm. of KI added, then excess of zinc sulphate or acetate, and the whole allowed to stand a few minutes. Sodium carbonate is now added until the solution is slightly alkaline, and the liberated iodine estimated by N/10 thiosulphate and starch. The zinc ferricyanide is thus converted into ferrocyanide, and the liquid remains of a milky white colour. The end reaction is sharp and decisive.

From the equation—



we see that one atom of oxygen is liberated, or the above weight, 1·1 grms., $K_3Fe(CN)_6$ would liberate 3·7 cc. oxygen. The difference between the oxygen liberated by the ferricyanide alone and the oxygen thus found corresponds to that required to oxidise the organic matter.

In an actual experiment 1·1 grm. $K_3Fe(CN)_6$ required 33·1 cc. thiosulphate for the liberated iodine.

The same quantity with 500 cc. water and proceeding as above required 17·1 cc. Hence 33·1 - 17·1 = 16 cc. were required for the organic matter.

1 cc. thiosulphate = 0·00008 grm. oxygen; therefore 0·00008 × 16 × 2 = 0·00256 part per litre, or expressed as parts per million 2·56.

By the moist combustion process of Wanklyn, 2·34 parts per million. Very concordant results were obtained. By the ordinary method 0·072 part per 100,000, or 0·72 part per million.

There are alternative methods, of course, for estimating the excess of ferricyanide. The method employed is very exact, and can be carried out in an ordinary evaporating dish, provided dust particles be excluded. A retort as used in Wanklyn's ammonia method would doubtless be advantageous. The oxidation is much more complete than by Tidy's process. The high molecular weight of the ferricyanide and the small volume of oxygen liberated tend to reduce errors of titration, &c., to a minimum.

Potassium ferricyanide is of course well known as an oxidising agent by all organic chemists, and it appears rather surprising that it has not been hitherto employed for the process of water analysis.

Perhaps this short communication will induce others to try the reaction in a more extended manner. I believe it to be a more exact method than Wanklyn's moist combustion process, which latter method is decidedly better than the one adopted by the Society of Public Analysts or its modifications. Further, I am of opinion that oxidation in an alkaline solution is preferable to that of Kubel

and Tiemann in acid solution employed so much on the Continent. I believe that this method or that of Wanklyn gives much more reliable results than that of Tidy.

5, Roseville Road, Harrogate,
June 29, 1914.

THE NATURE OF BASIC LEAD CARBONATE.

By EDWIN EUSTON.

IN an article "On the Composition of White Lead" (*Journ. of Industrial and Engineering Chemistry*, March, 1914), reasons were presented for the assertion that white-lead consists of a mixture of normal lead carbonate with a basic carbonate of lead of the composition $PbCO_3.Pb(OH)_2$. The purpose of the present paper is to consider the nature of the combination of the components of this basic carbonate of lead. The existing assumption in text-books on pigments is that, in basic carbonate of lead, the lead carbonate and the lead hydroxide are firmly united in actual chemical combination, but the results obtained in the experiments here to be mentioned indicate rather that the basic carbonate of lead should be considered as among those substances described by Zsigmondy ("Colloids and the Ultramicroscope," p. 68) as mixtures of colloidal substances which can, under certain conditions, act as chemical compounds. "Not only (*Ibid.*, p. 69) have colloid compounds or colloidal mixtures, in which two colloids are united, been erroneously described as chemical compounds, but so also have mixtures or adsorption compounds of crystalloids with colloids."

The fact that the lead hydroxide portion of basic lead carbonate is soluble in ammonium chloride solution but not in cane-sugar solution, indicates that the lead hydroxide is not present in mere mechanical mixture and yet is not so firmly held as to be properly considered in chemical combination. Direct evidence that the basic carbonate of lead is an "adsorption compound" is afforded by the fact that, in more than fifty trials, various samples of white lead and of lead carbonate, when treated with basic lead acetate solution at room temperature by stirring or agitation, invariably withdrew lead hydroxide from the solution and correspondingly gained in weight. In composition the samples before treatment ranged from 12·0 to 16·3 per cent CO_2 , and after treatment contained as low as 10·1 and 10·3 per cent CO_2 in extreme cases. The extent of the reaction under uniform temperature conditions is dependent on the basicity of the lead acetate solution, on the relative amounts of the sample to be treated and of the available lead hydroxide in the solution, and on the duration of the treatment. Merely enough agitation is required to ensure uniform treatment. The process proceeds slowly, requiring, for example, six hours in one instance to enable a sample containing 14·7 per cent CO_2 to join with enough lead hydroxide from the solution to reduce to 10·1 per cent CO_2 in the final product. Excess of basic lead acetate in solution beyond the calculated amount is required for complete action, as the end-point of the reaction is an equilibrium determined by the relative basicity of the solution and of the sample under treatment. With a sample containing both normal lead carbonate and basic lead carbonate, this equilibrium can be disturbed in either direction at will by the addition of a further quantity of basic lead acetate solution or by the addition of neutral lead acetate solution. Samples prepared from lead carbonate in the manner described respond to the tests for basic lead carbonate to the extent that their analyses indicate.

To learn whether normal lead carbonate is unique in its ability to withdraw lead hydroxide from basic lead acetate solution, similar trials, using considerable excess of basic lead acetate solution, were then made with kaolin, commercial zinc oxide, basic zinc carbonate, whiting, precipitated calcium carbonate, precipitated barium

sulphate, and precipitated barium carbonate. The kaolin gained 10.6 per cent in weight by addition of lead hydroxide, and two different brands of zinc oxide gained only 0.6 per cent each. The other substances named formed compounds corresponding approximately to the following formulæ:—

Basic zinc carbonate became $\text{ZnCO}_3 \cdot \text{Zn}(\text{OH})_2 \cdot 3\text{Pb}(\text{OH})_2$.

Whiting became $2\text{CaCO}_3 \cdot \text{Pb}(\text{OH})_2$.

Precipitated CaCO_3 became $2\text{CaCO}_3 \cdot \text{Pb}(\text{OH})_2$.

Precipitated BaSO_4 became $3\text{BaSO}_4 \cdot \text{Pb}(\text{OH})_2$.

Precipitated BaCO_3 became $3\text{BaCO}_3 \cdot 2\text{Pb}(\text{OH})_2$.

The calcium compounds and the barium sulphate compound were so lacking in opacity as to be worthless as pigments. The barium carbonate compound and the basic zinc carbonate compound showed marked improvement in density, in opacity, in brushing quality, and in rapidity of drying with linseed oil, in these respects closely resembling white-lead. In tinting and spreading power the basic zinc carbonate compound equalled white-lead, and the barium carbonate compound considerably exceeded it. These results show that other substances than normal lead carbonate form compounds with lead hydroxide from basic lead acetate solution, and that the lead hydroxide so combined tends to give to such compounds, in varying degree, characteristics as pigments heretofore ascribed only to white-lead. Further similarity is shown by the lead hydroxide portion of the compounds being soluble in ammonium chloride solution but not in cane-sugar solution.

The slow withdrawal of lead hydroxide from basic lead acetate solution by normal lead carbonate to form basic lead carbonate, the like action of some other substances in forming lead hydroxide compounds, the similarity in some properties conferred by the lead hydroxide on these different compounds, and the fact that the lead hydroxide is present neither in mechanical mixture nor in true chemical combination, indicate that basic lead carbonate is an adsorption compound.—*Journal of Industrial and Engineering Chemistry*, vi., No. 5.

THE CINEMATOGRAPH IN RESEARCH.

IN an extremely interesting lecture before the Fränkisch-Oberptälzischer Section of the Verein deutscher Ingenieure (*Zeitschrift des Ver. deut. Ing.*, 1914, lviii., 268), Dr. Ing. Hanz Goetz outlined the part cinematography had played in scientific and technical research and suggested some of the things that may be expected of it in the future. After an introduction giving statistics, describing apparatus, and outlining the history of the invention, the lecturer takes up the position of moving picture photography among the means of reproducing phenomena to the census. It differs from other means in that it correlates two of the basic quantities that physics deals with, time and extension in space.

The most obvious way in which the cinematograph may act as an aid to science is in recording rare phenomena, such as scenes in the life of seldom seen or difficultly accessible animals, unusual surgical operations, &c.—fields in which considerable success has been attained. Its usefulness only begins here, however. Just as the scale of objects may be varied when they are represented graphically, so the time scale of actions may be changed when they are represented by the cinematograph. By an increase in speed, Professor Pfeffer, of Leipzig, has been able to reproduce in three minutes a ten-day period of growth of a horse-chestnut twig; pictures for this reproduction were taken at five-minute intervals. A large field for the study of the growth of both plants and animals is thus opened up. Just as slow motions can be hastened so that it is possible to see the total effect in a truer perspective, so it is possible to retard and analyse quick movements, and the limits are only those of the speed

with which the pictures can be taken. With the most refined mechanical devices it is not possible to take more than 250 pictures per second, but by illuminating the moving object with regularly succeeding electric sparks and photographing on a film moving continuously rather than intermittently, it was found possible to increase the number of exposures to 2000 per second. Bull has studied the flight of insects in this manner.

From an engineering point of view the cinematograph has been most useful in studying projectiles and their effect on armour plate. Much higher frequencies had to be used than Bull obtained, and the apparatus employed differed from his in not using a mechanical interrupter; in series with the illuminating spark-gap was a large condenser, and in parallel with it a small one; the large condenser is charged by an induction machine, and when it is discharged the small condenser is alternately charged and discharged across the gap. The period of the alternations can be judged with fair accuracy by the tone. Since an explosion can take place in the five-thousandth part of a second, the speed of nine to fifty thousand exposures per second, obtained by this method, is sufficient to furnish interesting results. Since it is obviously impossible to have the camera near the object photographed, a special arrangement is used.

The cinematograph can also be used for making quantitative measurements of movements. The fall of a body has been studied by photographing on the same film the falling object and the hand of a chronograph, and in the same way the action of a steam hammer has been timed.

In these lines the cinematograph has just begun to be developed, and offers great possibilities in solving problems dealing with time and space in fields as wide apart as engineering and biology, and makes possible the study of motions so slow that it has hitherto been impossible to form conception of their whole meaning, or so fast that it has been almost impossible to form any conception of them at all.—*Journal of Industrial and Engineering Chemistry*, vi., No. 5.

GAS ANALYSES BY FRACTIONAL DISTILLATION AT LOW TEMPERATURES.*

By G. A. BURRELL and F. M. SEIBERT.

(Concluded from p. 5).

At Fig. 2 is shown a diagram of the various steps in the separation of a natural gas into its constituents by means of fractional distillation at low temperatures. It will be noted that the original volume of the sample was 1531.0 cc. The sample was first liquefied with liquid air, and a distillate of 1311.3 cc. obtained with the mercury pump. A residue of 219.7 cc. was left behind. Both the residue and distillate were again treated at the temperature of liquid air. From the residue there was obtained 9.9 cc. more of methane, but no residue remained behind upon treating the distillate of 1311.3 cc. The sum total of 9.9 cc. and 1311.3 cc. represented practically all of the methane and nitrogen in the natural gas sample. The distillate from the re-liquefaction of the residue contained no methane as determined by a further treatment at the temperature of liquid air.

After the methane had been separated there remained a residue of 209.8 cc., consisting of ethane and higher paraffin hydrocarbons. This residue was cooled at temperatures ranging from -140° to -125° C., and as much gas removed with the pump as possible. Ethane and some propane were obtained, 13.3 cc.; a residue of 76.5 cc. remained behind. The distillate was then cooled to temperatures ranging from -150° to -135° C. and a distillate

* Paper presented before the Spring Meeting of the American Chemical Society, April 7–10, 1914, by permission of the Director of the Bureau of Mines, U.S.A.

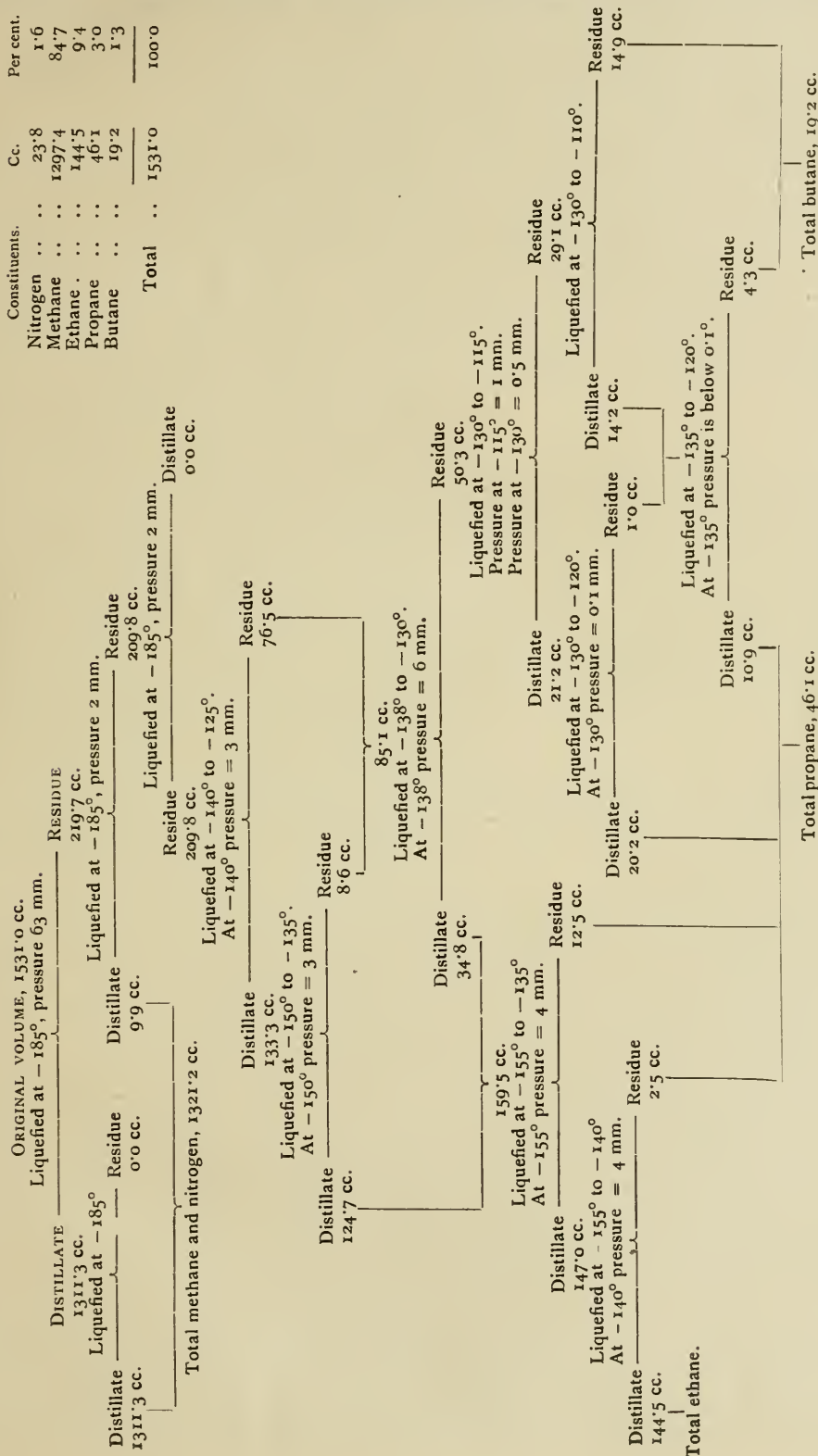


FIG. 2.—DIAGRAM SHOWING THE VARIOUS STEPS IN THE SEPARATION OF THE CONSTITUENTS IN NATURAL GAS BY MEANS OF FRACTIONAL DISTILLATION AT LOW TEMPERATURES.

of 124.7 cc. obtained and a residue of 8.6 cc. This 8.6 cc. residue was added to the 76.5 cc. residue, and the total, 85.1 cc., cooled to -138° to -130° and pumped. The distillate of 34.8 cc. was added to the 124.7 cc. distillate previously obtained, and total cooled at a temperature that did not rise above -135° C. There was obtained a distillate of 147.0 cc. and a residue of 12.5 cc. The 147.0 cc. distillate was then cooled and pumped at a temperature not higher than -140° C. The distillate, 144.5 cc., was found to be pure ethane. The residue from this last treatment, 2.5 cc., was added to the rest of the methane and ethane-free gas for the propane treatment. The separation of the propane and butane was carried on in a manner similar to the methane and ethane separations except for the use of higher temperatures.

Temperature measurements were made with two pentane thermometers. They agreed with each other, and gave for the melting-point of chloroform -62° C., of carbon disulphide -111° C., and boiling-point of fresh liquid air -193° C. The true melting-point of chloroform is -63.7° C., and of carbon disulphide -111.6° C.

Summary.

A method of separation of a natural gas into its paraffin hydrocarbons is shown. At a temperature of -185° C. to -190° C. the methane can be removed. The separation of the ethane from the propane, butane, &c., is conducted at temperatures ranging from 150° C. to -140° C. The propane is separated from the butanes, &c., at temperatures ranging from -135° C. to -120° C.

This method of separating a gaseous mixture into its constituents while somewhat involved is the only known method in the case of some hydrocarbons. It can be extended to the separation of other gaseous mixtures. The authors have separated other natural gases, but the example given herein is sufficient to describe the method.

SOME REACTIONS OF CHRYSOPHANIC ACID WITH REFERENCE TO ITS DETECTION IN COMPLEX MEDICINAL PREPARATIONS.

By E. MONROE BAILEY.

CHRYSOPHANIC acid, dioxymethylanthraquinone, $C_{15}H_{10}O_4$, is a yellow colour principle of weakly acid character occurring in a number of medicinal plants, notably in senna and rhubarb, and may be obtained also from its anthranol chrysarobin, $C_{15}H_{12}O_3$ (Liebermann, *Ber.*, 1888), which is present in Araroba or Goa powder (Oesterle, *Arch. Pharm.*, 1905, ccxliii., 434). The presence of the free acid in plants is presumably due to the enzymic hydrolysis of the glucoside, chrysophan. Chrysophanic acid is not the active principle of rhubarb, nor does the cathartic action of senna appear to be due primarily to its presence. It is soluble in alkalis with the production of a deep cherry-red colour. If the alkaline solution is heated with a little zinc dust reduction takes place and the red colour changes to yellow, the anthranol being formed (Allen's "Commer. Organ. Anal." 4th ed., vol. v., p. 208; cf., "Alizarin"). Re-oxidation in the alkaline solution takes place very readily; exposure to the air or simple dilution with water affects it, and a drop or two of hydrogen dioxide produces the change almost immediately. It behaves as an indicator, although its merits as such do not appear to have been investigated.

Toward reactions of oxidation chrysophanic acid appears to be quite stable. When taken into the body it may be, apparently, eliminated unchanged in the urine. It is said that after the ingestion of senna the urine becomes intensely yellow, and if rendered alkaline by sodium hydroxide a deep red colour is produced. Of nine men in this

laboratory, however, who took prescribed doses of senna—in preparations compounded with syrup of figs—in only two cases were positive tests given on examination of the urine twelve hours later. (These tests were made with commercial laxative preparations in which senna was declared to be an ingredient. The amounts of senna in many cases may have been too small to give the physiological test).

The applicability of chrysophanic acid for purposes of artificial colouring are apparent, one instance having been cited recently by Thum (*Am. Journ. Pharm.*, lxxxv., 1, 19). The sophistication of powdered rhubarb with powdered turmeric has been practised, and Howie and others have given some attention to the detection of curcumin in such cases (*Pharm. Journ.*, Nov., 1873; *Am. Journ. Pharm.*, 1874, iv., 1, 16). In the inspection of patented and other medicinal preparations, the detection of chrysophanic acid serves to indicate the presence of a restricted group of vegetable constituents. And, finally, the similarity of many of its reactions to those of phenolphthalein, a substance of not uncommon occurrence in medicines, makes its detection in presence of that substance desirable.

If an alcoholic extract containing chrysophanic acid is de-alcoholised or sufficiently diluted with water, acidified with a few drops of concentrated hydrochloric acid, and shaken out with ether (the emulsion which forms is readily destroyed by adding acetone), the colouring matter is taken up by the solvent, and the ethereal layer is coloured yellow. On washing the solvent with dilute alkali (2½ per cent ammonium hydroxide was used) the colour is transferred to the aqueous solution, which is coloured red. Similarly treated, picric acid and the colour principle of hydrastin yields no red colour to dilute alkali, nor does their presence interfere with subsequent tests; but curcumin, hæmatoxylin, and phenolphthalein yield colours not to be distinguished in certain concentrations from that produced by chrysophanic acid. In the cases of curcumin and hæmatoxylin, however, the colour of their alkaline solutions is slowly fugitive. After standing over night at $40-50^{\circ}$ the red element is entirely lost, but the red colour of chrysophanic acid and phenolphthalein is persistent.

If this solution is now acidified and shaken out with ether, the interfering colour principles, curcumin and hæmatoxylin, are eliminated. Their absence can be demonstrated by concentrating a portion of the ether shake-out on filter strips and testing as follows:—

1. Moisten one of the strips with a drop of strong hydrochloric acid. No pink colour will be obtained, showing the absence of hæmatoxylin.
2. Moisten another strip with a mixture of hydrochloric—boric acids. No red colour will be produced, showing the absence of curcumin.
3. Moisten a third strip with dilute ammonium hydroxide. A pinkish red colour will indicate the presence of chrysophanic acid or phenolphthalein or both.

To eliminate phenolphthalein transfer a portion of the ether shake-out obtained above to a test-tube and drive off the ether. Add a little zinc dust and 4–5 cc. of 25 per cent sodium hydroxide, boil until the red colour is discharged, and cool the solution. By this treatment chrysophanic acid is reduced, as already described, the solution becoming yellowish, and phenolphthalein is reduced to phthalin, which is colourless. Dilute the alkaline solution with water, or treat it with a few drops of hydrogen dioxide, and the characteristic cherry-red colour of chrysophanic acid will be obtained. Phthalin remains unoxidised under these conditions.

Curcumin and hæmatoxylin both undergo reduction by means of zinc dust and sodium hydroxide, and neither are subsequently oxidised by hydrogen dioxide, but their yellow or brown solutions mask the colour of chrysophanic acid in certain proportions and thus make the test for the latter less distinct. It is therefore best to eliminate these substances by the method described.—*Journal of Industrial and Engineering Chemistry*, vi., No. 4.

THE DETERMINATION OF MINUTE AMOUNTS OF SULPHUR DIOXIDE IN AIR.*

By ATHERTON SEIDELL and PHILIP W. MESERVE.

IN the case of most of the determinations of small amounts of sulphur dioxide in air, which have so far been made, considerable volumes of sample were available. Methods based upon the aspiration of a large amount of air through a small quantity of liquid, and the gravimetric estimation of the retained sulphur, could therefore be used. In such cases the results showed the average sulphur dioxide content for various periods of time. The problem at present in hand was the estimation of sulphur dioxide at any particular instant in the air of railway tunnels. (A detailed account of the analytical results obtained by the method here described will be given in a Bulletin of the Hygienic Laboratory, U.S. Public Health Service).

The approximate dilutions which were to be determined were ascertained by liberating given amounts of the gas in a closed room and noting the odour. It was found in this way that 10 parts per million produced an effect similar to that often experienced whilst passing through a smoke-filled railway tunnel.

In order to collect what might be termed instantaneous samples, use was made of evacuated 2.5 litre bottles. These were provided with seals made of short glass tubes passing through the stoppers. On breaking the tip of the tube, the air entered within a few seconds, and therefore constituted a fairly representative sample of the atmosphere at the particular point at which the seal was broken. It therefore became necessary to determine in 2.5 litre samples of air, amounts of sulphur dioxide varying from about 0.0025 to 0.05 of a cubic centimetre.

The determination of fairly large amounts of sulphur dioxide by iodometric titration can, of course, be made with considerable accuracy. The application of this method to the determination of very small amounts of the gas appeared to be simply a question of ascertaining the peculiarities of the iodine reaction at great dilution, and selecting those conditions most favourable to constancy and accuracy of results. Experiments were made with dilutions of sulphur dioxide of the order of magnitude under consideration, namely, one to twenty parts per million. The titrations were made in the 2.5 litre white glass bottles, using N/1000 iodine and thiosulphate solutions. In those cases in which an excess of iodine was used and the end-point approached with thiosulphate, great difficulty was experienced in judging when the last trace of the blue colour of the starch disappeared. It was also found that even in the absence of sulphur dioxide, direct titrations with iodine and thiosulphate solutions gave quite different results, depending upon whether the end-point was approached from the side of appearance or of disappearance of the blue colour of the starch indicator. This point showed that no method of determination of very small amounts of sulphur dioxide involving a back titration would be practicable.

The results of the extended series of experiments showed that satisfactory determinations can best be made by adding 5 cc. of 0.1 per cent aqueous starch paste to the bottle containing the sample, and after rotating in such a manner that the interior walls are entirely moistened, titrating with N/1000 iodine solution to appearance of the blue colour of the starch iodide. The end-point obtained in this manner is quite sharp, one or two drops of the iodine being sufficient to produce the final distinct blue colour. Blank titrations made in exactly the same manner in a bottle containing air free from sulphur dioxide, required an average of 0.3 cc. N/1000 iodine to yield an equivalent colour change in the aqueous starch solution. This correction must therefore be applied to the titrations made

upon samples containing sulphur dioxide. Since the reaction between iodine and sulphur dioxide is represented by the equation $I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4$ and 1 litre of SO_2 at 0° and 760 mm. pressure weighs 2.862 grms., then 1 cc. N/1000 iodine should correspond to 0.000032 gm. or 0.0112 cc. SO_2 (at 0° and 760 mm.). In order to test the reaction at great dilutions the titrations of given mixtures of air and sulphur dioxide as shown in Table I. were made.

TABLE I.—Results of Direct Titration of Mixtures of Sulphur Dioxide and Air with Standard Iodine Solutions.

Composition of mixture.		Cc. standard iodine (corr.).	Calculated volume SO ₂ .	Per cent of actual SO ₂ found.	
Cc. air.	Cc. SO ₂ .*				
3875	1.8	13.35	N/100	1.49	83
250	1.8	13.5	"	1.51	84
3875	0.9	6.55	"	0.73	81
250	0.9	6.8	"	0.76	84
3875	0.9	6.75	"	0.76	84
250	0.9	6.7	"	0.75	83
3875	0.36	2.65	"	0.30	83
250	0.36	2.85	"	0.32	89
3875	0.36	2.75	"	0.31	86
250	0.36	2.75	"	0.31	86
3875	0.09	6.95	N/1000	0.078	87
250	0.09	7.25	"	0.081	90
3875	0.09	6.85	"	0.077	86
250	0.09	7.0	"	0.078	87
2500	0.09	6.8	"	0.076	84
2500	0.09	7.5	"	0.084	93
2500	0.09	6.9	"	0.077	86
2500	0.09	7.1	"	0.080	88
2500	0.09	7.5	"	0.084	93
2500	0.09	7.25	"	0.081	90
2500	0.09	6.55	"	0.073	81
2500	0.018	1.15	"	0.013	72
2500	0.018	1.05	"	0.012	66
2500	0.018	1.15	"	0.013	72
2500	0.018	1.1	"	0.012	68
2500	0.018	1.1	"	0.012	68
2500	0.009	0.8	"	0.009	98
2500	0.009	0.6	"	0.007	75

* At 0° and 760 mm.

The sulphur dioxide was measured by successively diluting a given volume of the pure gas with air and transferring definite amounts of the mixture to partially evacuated bottles of the capacity indicated in the table under "Cc. Air."

An examination of this table shows that in all cases low results are obtained. The average for concentrations of SO_2 between 0.09 and 1.8 cc. is 86 per cent, and for concentrations below 0.09 (except Det. No. 27) it is 70 per cent. There are two possible explanations for the low results. Either the reaction of the iodine with the sulphur dioxide may be incomplete at this dilution or else partial oxidation of the sulphur dioxide occurs when it is diluted with air. Some evidence upon the latter of these assumptions is contained in the table. Thus it will be seen that in practically all of the duplicate titrations made in large and in small bottles, slightly lower results are obtained in the larger bottles, that is, in the more highly diluted mixtures. Also the percentage of sulphur dioxide recovered is lowest in the case of the more dilute mixtures. It may therefore be concluded that some oxidation takes place simply upon allowing sulphur dioxide to diffuse in a large volume of air of ordinary dryness.

In regard to the incompleteness of the reaction, it was pointed out by J. Volhard (*Liebig's Annalen*, 1887, ccxlii., 93) many years ago that in titrating aqueous sulphurous acid solution with standard N/10 iodine, less sulphur dioxide is found when the titration is made with the iodine, that is, to appearance of the blue starch colour, than when made in the reverse direction. At 1/10

* Presented at the Rochester Meeting of the American Chemical Society, September 9, 1913. From the *Journal of Industrial and Engineering Chemistry*, vi., No. 4.

normal concentrations the difference amounted to about 5 per cent of the sulphur dioxide present. Results for more concentrated solutions are given, but none for solutions more dilute than 1/10 normal.

In order to obtain data upon this point an experiment was made by us as follows:—A standard solution of sulphur dioxide was prepared by dissolving an accurately measured volume of the gas in distilled water and diluting to a known volume. The first dilution contained 1.097 grms. SO_2 per 1000 cc. The second dilution contained 0.1097 grm. SO_2 per 1000 cc.

a. Titrations made with the first dilution and N/10 iodine:—

10.38 cc. N/10 iodine required 35.05 cc. SO_2 solution = 98.6 per cent SO_2 found.

35.05 cc. SO_2 solution required 9.96 cc. N/10 iodine = 83.0 per cent SO_2 found.

b. Titrations made with second dilution of SO_2 solution and N/100 iodine:—

10.1 cc. N/100 iodine required 32.3 cc. SO_2 solution = 91.5 per cent SO_2 found.

32.3 cc. SO_2 solution required 9.54 cc. N/100 iodine = 86.2 per cent SO_2 found.

c. Titrations made with second dilution of SO_2 solution and N/1000 iodine:—

50.0 cc N/1000 iodine required 15.75 cc. SO_2 solution = 92.5 per cent SO_2 found.

15.0 cc. SO_2 solution required 43.6 cc. N/1000 iodine = 83.7 per cent SO_2 found.

Although these results are not perfectly consistent, they show that the titration to appearance of the blue colour of the starch indicator gives the lower results, and the actual percentage recovered is approximately equal to that found by titrating the sulphur dioxide and air mixtures in the large 2500 cc. white glass bottles, as reported in Table I.

A more detailed study of this incomplete recovery of sulphur dioxide by iodine titration would be of considerable interest, but further experiments were not made by us, since it was evident that for the purpose of the present investigation of tunnel air, greater accuracy was not required.

From a consideration of the above experiments it is evident that a correction factor for incompleteness of the reaction at the great dilutions must be applied to the iodine titrations. The selection of this factor was based upon the results shown in Table I. Here it is seen that for concentrations between about 4 and 40 parts per million the recovered sulphur dioxide lies between 70 and 86 per cent. It was therefore concluded that the factor 1.3 would bring the results sufficiently near 100 per cent for all practical purposes.

There is one other point which must be taken into consideration in connection with the determination of small amounts of sulphur dioxide, and that is the rate of loss due to oxidation, on standing. It was early noticed that the presence of moisture hastens this loss very materially. Even in the case of bottles dried as carefully as possible and with the exercise of reasonable precautions to exclude moisture, it was found that the sulphur dioxide began to disappear within a short time. Some experiments were therefore made for the purpose of ascertaining how soon the titrations of given samples must be made in order that loss due to oxidation may be avoided. A series of experiments was first made with carefully dried bottles. The results are shown in Table II.

In the case of the dry bottles it would appear from the results that the disappearance is the more rapid the more dilute the sulphur dioxide. This, however, cannot be definitely concluded since the experiments with the moist bottles indicate that the moisture factor plays a much more important part than the concentration. The difference in rate of loss as shown by the first series of seven determinations and the second series of eight determinations in

Table II., may, in fact, be due to inappreciable differences in moisture content of the laboratory air with which the dilutions were made in the two cases, rather than to the 50 per cent difference in concentration of the sulphur dioxide itself.

TABLE II.—Showing Rate of Disappearance of Sulphur Dioxide from Dilute Mixtures with Air in Dry 2500 cc. Bottles.

Volume of contained SO_2 (at 0° and 760)	Time of standing. Minutes.	N/1000 iodine (cor.) Cc.	Found vol. SO_2 (at 0° and 760) Cc.	Per cent SO_2 recovered.
0.09	10.0	6.45	0.094	104
0.09	20.0	6.75	0.098	109
0.09	65.0	3.6	0.052	60
0.09	90.0	6.3	0.092	100
0.09	135.0	5.15	0.075	83
0.09	160.0	4.5	0.065	72
0.09	225.0	2.85	0.042	47
0.045	0.5	3.1	0.045	100
0.045	14.0	2.55	0.037	82
0.045	30.0	1.6	0.023	52
0.045	45.0	0.95	0.014	31
0.045	60.0	1.35	0.019	43
0.045	75.0	1.25	0.018	40
0.045	100.0	1.55	0.022	50
0.045	130.0	1.55	0.022	50

In the experiments with moist bottles the irregularities were so great that no conclusion in regard to the rate of oxidation of the sulphur dioxide could be drawn. In some cases about half of the added gas had disappeared within a few minutes, and in others a loss of only about 30 per cent had occurred in half an hour. In practically all cases only a small fraction of the used sulphur dioxide was recovered after one hour. These irregularities were found even in spite of special efforts to maintain uniform conditions for the experiments. The results demonstrated the necessity of using dry bottles for collecting the samples. They also indicate that except on very dry days it is necessary to make the titration within less than half an hour after collecting the samples in order to avoid low results due to gradual oxidation of the sulphur dioxide.

In order to test further the direct iodine titration method for sulphur dioxide, several series of determinations were made upon samples of air from a room in which given volumes of pure sulphur dioxide were liberated. The room was 9 ft. $\times$ 10 ft. $\times$ 13 ft. = 1170 cubic feet capacity and contained a rather large window and door. The walls were of painted plaster. No attempt to seal the cracks around the window and door was made. A large electric fan was arranged to cause a rapid circulation of the air in the room. For each experiment the given volume of sulphur dioxide was liberated quickly, and after a two to six minute period of stirring with the fan, the seals on the first series of eight evacuated dry bottles placed near together on a table were broken practically simultaneously. A second series of six samples were taken after an additional five to ten minutes' stirring. These samples were titrated as quickly as possible in all cases. The analytical results are given below in the order in which the titrations were made:—

Experiment I.—Volume of SO_2 liberated = 500 cc. or, on the basis of the volume of the room, 15 parts SO_2 per 1,000,000. *First series* of samples taken after two minutes' stirring contained, respectively: 5.0, 7.9, 6.4, 4.1, 1.9, 5.5, 0.9, 5.5 parts SO_2 per 1,000,000. *Second series* of samples taken after six minutes' stirring contained, respectively: 7.6, 6.0, 5.5, 6.7, 4.1, 5.5 parts SO_2 per 1,000,000.

Experiment II.—Volume of SO_2 liberated = 500 cc. or 15.0 parts per 1,000,000. *First series* of samples taken after five minutes' stirring contained, respectively: 10.0, 9.9, 7.0, 5.0, 9.6, 1.2, 6.1, 5.8 parts SO_2 per 1,000,000. *Second series* of samples taken after ten minutes' stirring con-

tained, respectively: 6.1, 6.1, 5.8, 4.1, 4.7, 5.8 parts SO₂ per 1,000,000.

Experiment III.—Volume of SO₂ liberated = 500 cc. or 15.0 parts SO₂ per 1,000,000. There were also liberated 3300 cc. of CO₂ (=100 parts per 1,000,000) generated by mixing aqueous Na₂CO₃ and H₂SO₄ solutions. The weather outside was cloudy and moist. *First series* of samples taken after five minutes contained, respectively: 3.5, 2.3, 1.8, 6.4, 3.2, 2.6, 1.2, 1.2 parts SO₂ per 1,000,000. *Second series* of samples taken after ten minutes contained, respectively: 4.6, 7.0, 2.3, 1.8, 3.8, 3.2 parts SO₂ per 1,000,000.

Experiment IV.—Volume of SO₂ liberated = 213 cc. or 6.4 parts per 1,000,000. *First series* of samples taken after three minutes contained, respectively: 5.2, 2.3, 1.2, 1.2 parts SO₂ per 1,000,000. *Second series* of samples taken after six minutes contained, respectively: 3.2, 2.3 parts SO₂ per 1,000,000.

It will be noted that in all cases considerably less sulphur dioxide was recovered than liberated. There appears to be an initial loss amounting to about 30 to 50 per cent of the liberated gas. The variation between the individual samples of the second series in each case is less than for the first series, due probably to the more thorough mixing after the longer period of stirring. The variations between the several experiments are very significant. Thus in Experiment III., made on a cloudy, damp day, and in which considerable water vapour was set free during the generation of the carbon dioxide, the recovered sulphur dioxide is appreciably lower than in the case of Experiments I. and II. The moisture content of the air, therefore, influences the loss of sulphur dioxide set free in the room to a very considerable extent.

Summary.

It has been shown that very minute amounts of sulphur dioxide in 2½ litre samples of air can be determined by direct titration with N/1000 iodine. A correction factor of 1.3 for the apparent incompleteness of the reaction at the great dilution must be applied. On account of the gradual oxidation of the sulphur dioxide, the titrations must be made within a short time after the collection of the sample. The presence of moisture hastens the loss by oxidation very materially.

HOW TO IDENTIFY ROSIN AND GLUE SIZINGS.

IN a contribution from the Royal Testing Laboratories of Germany, which is abstracted briefly in the *Papierfabrikant*, Prof. W. Herzberg draws attention to the work of Kollmann on the testing of papers for the detection of rosin and animal sizes. Kollmann has determined the behaviour of papers in the presence of various reagents, including iodine solution, concentrated nitric acid, nitrate of mercury, potash lye, and sulphate of copper (biuret reaction), glacial acetic and concentrated sulphuric acid (Adamkiewicz), tannin solution, concentrated sulphuric acid and sugar (Raspail's reaction). Only Raspail's reaction and the tannin reaction were found useful, and these only in the absence of fat and casein.

The Raspail Test.—The Raspail test depends on the fact that proteids, rosins, fats, &c., turn rose-coloured or violet under the action of concentrated sulphuric acid and a little strong cane-sugar syrup. Animal size shows the reaction much weaker than rosin size, so that the reaction only comes into question for the recognition of the latter. The test can only be carried out satisfactorily under the microscope.

The procedure is to dampen a little scrap of paper with

the sugar solution, put it on the slide, free it from excess of sugar by lightly pressing blotting-paper on it, and then to add the strong sulphuric acid when the paper is already under observation with a low power. In this case nothing much will be seen if the sizing is animal, but with rosin sizing a deep red colour will appear at the parts of the paper attacked by the acid.

The Tannin Test.—Tannin precipitates animal size. If a piece of paper is wetted and stuck on the slide, and warmed, the paper being then removed, and tannin solution added to the aqueous extract left on the slide, no precipitate appears if the size was rosin, but a voluminous brown deposit, readily observed as it appears through the microscope, is formed in the case of animal size.

Extraction Tests.—Some of the other tests commonly employed in the determination of rosin and glue in papers are as follows:—The United States Bureau of Standards determines the rosin quantitatively. A 5 gm. sample of paper is cut into strips and the paper folded back and forth upon itself, and then placed in a 300 cc. Erlenmeyer flask. The paper is extracted with alcohol made acid with acetic acid.

The extract is next transferred to a casserole, and after evaporating off the alcohol, the acid residue is taken up in water and extracted with ether in a separatory funnel. Three extractions are sufficient, and the combined ether extracts are washed twice with water and transferred to a weighed dish. After evaporation to dryness the residue is evaporated with absolute alcohol to remove water and heated in an air-bath at 90° C. for one hour.

The dish is then allowed to cool in a desiccator and weighed. The resultant weight in grms. divided by 5 and multiplied by 100 gives the per cent total rosins.

One of the simplest tests for the presence of rosin sizing is to place a drop of ether on the paper. The presence of rosin sizing will be indicated by the formation of a ring around the edge of the spot after the ether has evaporated.

A quantitative determination for glue may be made by extracting a sample of the paper with warm water and precipitating the glue with tannin or phosphomolybdic acid. The precipitate that forms is an indication of glue in the paper.

Of the foregoing test, described as used by the Bureau of Standards, Kollmann says that a test of this kind which depends on extracting rosin from paper with solvents that will not dissolve animal sizes, has, like the Kiliani test, failed so completely as to be negligible.

The Iodine Test.—The iodine test is approved by Kollmann. Albuminous bodies, which include animal glues, give with iodine solution either direct or, on acidifying with acetic acid, yellow or brown colourations or precipitates. The iodine solution is made by dissolving as much iodine in a 1 per cent solution of potassium iodide as possible. The reaction must be observed not only with the sized fibre, but with an aqueous extract of the paper. If some of the paper, teased out with a needle on the slide, is dabbed with the solution, a brown colour is produced, whether the sizing is rosin or animal. If, however, the paper is heated on the slide with a little water, and then removed, the dried residue on the slide shows characteristic appearances under the microscope and even under a good hand lens.

Animal-sized paper leaves behind a considerable structureless residue extending over the whole surface formerly occupied by the water. The iodine solution gradually dissolves it with a rusty red colour. On the other hand, rosin-sized paper leaves but little residue, and that shows a grainy structure with an irregularly dented edge round the space formerly taken up on the slide by the aqueous solution. This residue also gives a brown colour with the iodine solution. It consists of free abietic acid, melted out by the hot water, and forming an irregular deposit against the dry part of the glass.

The Xanthoprotein Reaction.—The nitric acid

affords the so called xanthoprotein reaction, albuminous bodies giving a more or less pronounced yellow colour after heating with nitric acid and subsequent exposure to ammonia. Many rosins and alkaloids react similarly. The test is applied as follows:—A small piece of the paper is treated on the microscope slide with strong nitric acid, carefully dried, and then treated with ammonia. If the paper was sized with animal size, the yellow will be deeper. The difference is small, but with practice it can be safely used to distinguish between animal and vegetable size.

The Millon Test.—When warmed with this reagent (a solution of mercuric nitrate containing nitrous acid) all albuminous bodies, and, therefore, animal size, are coloured red, from a light pink to a deep brick red. The reagent is best prepared shortly before use by dissolving one cubic centimetre of mercury in 9 cc. of nitric acid of 1.52 sp. gr., and diluting the solution with 10 cc. of distilled water. The test is applied as follows:—To a few drops of the solution in a watch-glass add just the smallest possible fragment of sodium nitrate, to insure the presence of enough nitrous acid. A drop is then transferred by means of a glass rod from the watch glass on to a scrap of the paper to be tested on the slide, which is then carefully heated. In the presence of albuminous bodies, the paper turns red, the shade being pale or dark according to the amount of size present. The red soon changes, however, to a dirty brown, and if the Millon reagent is not fresh, the characteristic pinks and reds may be lost altogether. This yellowish brown is the only colour produced by the reagent in the case of rosin size. This test, too, is only reliable in experienced hands.

The Adamkiewicz Test.—If albuminous bodies are warmed with a mixture of two parts of glacial acetic acid and one of concentrated sulphuric acid, many of them give a strong red or violet colouration. Casein shows this reaction, animal size does not. This test can only be applied to an extract made from the paper with dilute potash. The paper is wetted with the lye on the slide, and then removed with a needle. The remaining liquid is made acid with acetic acid, and warmed to coagulate the casein. This is then washed by alternate moistening with water and pressing with filter-paper. It then gives the colour with the mixed acids.

The Biuret Test.—Albuminous bodies treated first with caustic potash lye, and then with solution of sulphate of potash, give colourations of red and violet. The value of this test consists in the fact that it gives a fully negative result with rosin size. This test is also best tried under the microscope. A little bit of the paper is wetted on the slide with caustic potash lye of about 10 to 15° B., and after a minute or two has been given to enable the caustic alkali to dissolve the size, one drop of a 2 per cent solution of copper sulphate is added from the end of a glass rod. The violet shows best in the fibre after the slide has been drained by setting it on edge.

Kollmann advises that the tests should be carried out on the stage of the microscope whenever possible, so that the colours and precipitates can be observed as they form. The colours are very fugitive, especially under the strong light from the mirror below the stage. If the presence of both sorts of size is suspected, care must be taken to test for them on different portions of the paper.—*Chemical Engineer*, xix., No. 5.

THE PRESENT STATE OF THE CYANAMIDE INDUSTRY.*

By E. J. PRANKE.

CYANAMIDE is a dry greyish black pulverised material, which is made by combining pure atmospheric nitrogen with calcium carbide at a temperature of 1100 to 1200° C. Its principal use in this country is as a source of nitrogen in mixed fertilisers.

Fertilisers have an intimate relation to the cost of living that should be more generally recognised. It is a well known fact that the cost of living has increased in this country at a much more rapid rate than it has abroad. When we consider the facts closely, we find that the extraordinary increase in this country has been in the cost of food products, while other than foods have increased at only the general rate prevailing throughout the world. From 1900 to 1910, for instance, all commodities in this country increased in cost about 26 per cent, as compared with 9 per cent in England, and 12 per cent in France, or 15 per cent in the world, including the United States. But other than foods in this country increased only 17 per cent, while foods increased 35 per cent, or more than twice as much. While population increased 21 per cent in the ten years, crop production increased only 10 per cent.

The rapid increase in the cost of foods in this country must be checked by increased crop production, just as food prices are held down in the more densely populated European countries; the yields per acre must be increased. In Europe the yields of the staple crops average from 50 to 100 per cent larger per acre than in this country. Crop rotation, seed selection, and thorough cultivation are estimated to be responsible for one-half the increased yields, while the use of fertilisers is considered, by competent authorities, to cause as much increase as all other factors put together. The countries of highest agricultural development are the largest consumers of fertilisers. Germany, for instance, spends as much money per annum for fertilisers as we do, although she has only 1/13th of the acreage under cultivation that we have. This, moreover, is in a country of abundant cheap farm labour, which would indicate that mere muscle cannot take the place of plant food in the growing of crops.

The development of an increased use of fertilisers in this country is mostly a matter of education of the farmer, and to some extent a matter of fertiliser prices. The farmer must be taught that there is a right way and a wrong way to buy and use fertilisers, and that the right way is profitable; the wrong way may or may not be. A lower price, however, will always make it easier to earn a profit, and the lower the price the larger the profit, the greater the incentive to use fertilisers, and the larger the crops produced. Hence, any improvement in the art of manufacturing fertilisers or fertiliser materials that will make them cheaper, will ultimately lower the cost of foods, and hence the cost of living.

Any considerable reduction in the cost of fertilisers is hardly to be expected, however, unless it takes place through a reduction in the cost of the most expensive ingredient, nitrogen. The price of phosphoric acid is now probably about as low as it will ever be. The main source of this ingredient, namely, phosphate rock, is found in enormous deposits that will last a great many years. The present method of treatment would seem to be about as economical as any that is likely to be devised. So with potash. Practically all of our potash is imported from Germany, where it occurs in great natural beds that will last for many thousands of years at the present rate of development. It is true that lately there has been considerable talk of obtaining potash by the incineration of a seaweed, known as kelp, found in abundance on the Pacific

* Presented before the Nashville, Tenn., Section of the A. C. S., February 20, 1914. From the *Journal of Industrial and Engineering Chemistry*, vi, No 5.

Royal Institution. — A General Meeting of the Members of the Royal Institution was held on the 6th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Mrs. Walter Beevor, Mr. G. G. Blake, Mrs. W. H. Crocker, Mr. and Mrs. K. P. Hawksley, the Hon. Geoffrey L. Parsons, Mr. E. Sanger Shepherd, and Miss H. C. Schott were elected Members.

cost. Whether potash from this source can be produced and shipped to the eastern part of the United States at a much lower cost than the German potash can be delivered remains to be seen. A pound of nitrogen costs about four times as much as a pound of phosphoric acid or a pound of potash. The cost of the nitrogen in the average fertiliser makes up about 45 per cent of the total cost. The higher price paid for nitrogen, however, is justified by the fact that this is the element usually most needed to increase the productivity of the average soil, and, moreover, its application seems to be in most cases a prerequisite for the effective utilisation of the other ingredients, phosphoric acid and potash. A typical instance is found in the results of fifty five years of continuous experiments on wheat in England, at the Rothamsted Experiment Station. These are as follows:—

Fertiliser.	Bushels per acre.	
	Yield.	Increase.
None	12·9	—
Phosphate and potash only	14·8	1·9
Nitrogen only	20·5	7·6
Nitrogen, phosphate, and potash	31·6	18·7

Fertiliser nitrogen may be classified according to its sources, into organic, derived from animal or vegetable matter, and inorganic, derived from mineral sources. The price of the organic ammoniates, chief of which are cottonseed meal, tankage, dried blood, and dried fish, is steadily tending upward. This is due principally to the decreased per capita production of animal and vegetable products in recent years, and to the increased uses to which by-products are applied. Recently, the above by-products were used mostly in fertilisers, now they are used to a considerable extent in stock foods. The inorganic ammoniates, chief of which are sodium nitrate, ammonium sulphate, and cyanamide, have lately been suffering a general decline in prices. The general price level of this class of nitrogen is about the same as it was ten years ago, in spite of the increase of about 26 per cent in the cost of all commodities in that time. The lower prices now prevailing are undoubtedly due to the rapidly increasing production of inorganic ammoniates. Probably the most important single factor in this movement is the production of cyanamide.

In this country the demand for cyanamide has kept pace with the supply at the current prices for inorganic ammoniates, and sometimes at higher prices. Yet, this fact has led some of those who stand in the position of advisors to the farmer to assert that they cannot recommend a new material until its advantages have been proved superior, and in addition its prices made lower than that of the older ammoniates. They overlook the fact that no industry in the early stages of its development has turned out as perfect a product at as low prices as was later found possible. Pioneering is always costly, and a pioneer industry must have the support of the public from the start in order to develop at all. It is the history of great manufacturing enterprises that where the support of the public has been accorded, the final benefits to the public are out of all proportion to what could have been expected in the beginning. The only question that broadminded men should ask is:—Has the process inherent merit? Will it prove to be a great public good? With regard to the cyanamide process the answer must be:—Yes. The cyanamide process is probably the cheapest known process for producing a commercial nitrogen compound on a large scale. It is only a question of time until an ideal product is developed and sold at the lowest prices. In the meantime, however, the industry must have the support of the public. Fortunately, it has this support now, as is evident from a glance at the statistics.

In 1904 the world's production of cyanamide was 5000 tons. In 1909 it was 50,000 tons. In 1914 it will be 275,000 tons. The American Cyanamide Company began

operations at Niagara Falls in January, 1910, with a capacity of 12,000 tons per annum. This was increased in 1913 to 32,000 tons per annum. Further extensions, which will reach completion in April, 1914, will make the yearly capacity of the American plant 64,000 tons. The world's output of cyanamide brings at wholesale prices about 14,000,000 dols. per annum, the European product being of somewhat higher nitrogen content than the American.

Now if one were to turn to the literature on cyanamide, and on the basis of what he reads there hazard an opinion as to the rate of growth of the industry in the past ten years, he would probably fall far short of the truth in his estimate. If the literature were taken by the public as the sole basis of judgment of the value of cyanamide as a fertiliser, it is doubtful whether there would be enough cyanamide sold to keep one small factory busy furnishing the world's supply, instead of the fourteen large factories with their output of 14,000,000 dols. worth of product per annum. It is conceivable that a small amount of an inferior material might be disposed of by clever salesmen for one or two seasons, but the fact of such steady rapid growth as the cyanamide industry has made is inconsistent with essential inferiority. The fact is, that the great majority of limitations that have been attributed to cyanamide simply have no bearing upon the practical use of the material. Some of the limitations mentioned in the literature do not exist at all, while the practical significance of others is found, on examination, to approach zero in value.

Advancement in the knowledge of a substance begins when its properties are expressed quantitatively. Practically all of the problems of the early days of the cyanamide industry have been solved by paying attention to the quantities involved. Let us now consider some of the characteristics of cyanamide that have been claimed in the literature to be disadvantageous, and let us note in each instance how the supposed difficulty was solved.

Calcium Carbide.

This substance was occasionally found to the extent of several per cent in the material produced in the earlier days of the industry abroad. It is now entirely removed in the course of manufacture by the addition of sufficient water to entirely decompose it. The American practice of hydration, makes the presence of undecomposed carbide impossible. In Europe, the last step before shipping the material is to test for carbide.

Change in Weight and supposed Loss of Nitrogen in Storage.

On exposure to the air, cyanamide absorbs moisture and carbon dioxide, which makes it weigh more. As the total weight increases, the percentage of nitrogen will of course decrease. The new weight, however, multiplied by the new percentage of nitrogen will show the same number of pounds of nitrogen present after storage as there was at the beginning. Early observers noted the decrease in nitrogen analysis, but failed to take account of the increase in weight; hence they reported large losses of nitrogen. All attempts, however, to show a loss of nitrogen in goods stored in factories have failed, when the final weight of the pile was determined, as well as the analysis of a sample drawn in a uniform manner from all parts of the pile. When storage is desirable and necessary, it is a relatively simple operation to draw a practical average sample for analysis at the conclusion of the period of storage. It should be mentioned here too that other fertiliser materials are by no means perfect in respect to their storing qualities. The practical man, however, does not ask for perfection; it is usually too difficult of attainment, and too costly and often quite useless. All that is required is that a thing be good enough for the purpose.

It is true that laboratory experiments have shown that when a few grms. of cyanamide are exposed in a thin

layer to a constantly saturated atmosphere of moisture for a long time an odour of ammonia is given off, and a loss of about 0.02 per cent of the total nitrogen for each 1 per cent gain in weight of the exposed sample can be detected after allowing for the increase in weight. It is doubtful, however, whether this has any practical significance. The fact that iron filings will rust overnight in a damp atmosphere does not prevent the use of iron for building bridges or other structures exposed to damp weather. The fact that iron filings are readily burned by dropping them through the flame of a match has not prevented the use of iron as a non-combustible building material. Even assuming that the severe conditions of the laboratory experiment with cyanamide could be applied to conditions of factory storage, the loss of nitrogen would be insignificant. In factory storage cyanamide gains in weight on an average only about 1 per cent a month. Hence a material containing 16 units of nitrogen would contain, after one month, between 15.997 and 16.000 units. To the practical fertiliser man such differences are inappreciable. Even in one year, at this rate, the loss would be only 0.036 unit of nitrogen. The best fertiliser analyses for nitrogen, however, have no meaning within 0.100 per cent, and sometimes 0.200 per cent. As a matter of fact the immaterial loss of actual nitrogen from cyanamide is probably much less than the actual losses known to occur in the decomposition of organic fertiliser materials in storage. All these are so insignificant that nobody pays any attention to them.

(To be continued).

THE THEORY OF COMPRESSIBLE ATOMS.*

By THEODORE W. RICHARDS.

SPECULATION concerning the ultimate nature of matter goes far back into the early history of mankind. As soon as several of the ancient Greek philosophers perceived that some kind of atomic hypothesis is the simplest method of accounting for things, they attempted to imagine the nature of the ultimate particles. The apparent permanence of the Universe suggested that these particles could never become worn out, and hence the ancients naively conceived of them as being infinitely hard. Newton inherited this idea, and spoke more than once of "hard massy particles." Not much over a hundred years ago, Dalton brought forward convincing quantitative evidence in favour of the atomic theory, putting it thus upon a firm basis; and the theory was later adopted by physicists to explain the pressure of gases. Throughout these considerations the ancient notion of hard, incompressible, but perfectly resilient, atoms persisted—partly because this assumption served as a convenient basis for mathematical analysis.

According to the tenets generally held during the last fifty years, solids and liquids, as well as gases, are supposed to be constituted of small hard atoms (or complexes of hard atoms called molecules) with wide empty spaces between them—these atoms being supposed to be each for itself in violent irregular motion to and fro, due to heat. There is, however, nothing in this philosophy to distinguish solids and liquids from gases, although in reality they are very different indeed. Such a conception gives a very reasonable picture of the state of a gas, but does not explain the fixed bulk of liquids nor the rigidity and impermeability of solids. To overcome these difficulties it was necessary in discussing solids and liquids to add to the hard imaginary incompressible particle a magic "sphere of influence" surrounding it, which would prevent its

touching other atoms; but how this "sphere of influence" was constituted no one was quite prepared to say.

About fourteen years ago in studying the behaviour of gases, I came to the conclusion that even with this dilute form of matter, the imaginary particles (although here widely separated) were still surrounded by "spheres of influence," somewhat but not very much larger than those imagined to exist in liquids; and it seemed that since a "sphere of influence" appears always to accompany the atom, the little hard particle in the middle might have no real physical significance; this imaginary hard particle appeared to be a purely arbitrary assumption. The so-called "sphere of influence" in all its relations acts as if it were really the important thing to be considered. Hence the question was proposed: Why should we not call this sphere of influence the atom itself, since it always accompanies the atom, and why should we pretend to know anything about how the material is distributed within its limits? The gain in this point of view is twofold. In the first place it concentrates the interest and attention upon the entity which actually comes into consideration; on the other hand, it abolishes an arbitrary hypothesis.

If we consider the "sphere of influence" as being the practical boundary of the atom, we must call the atom compressible; for the "sphere of influence" is compressible; in other words, liquids and solids are actually compressed when pressure is applied to them. If the atom is compressible and elastic throughout its substance, we may imagine vibration within it; thus heat may be explained even in closely packed atoms of this kind.

One can easily see that the new hypothesis is suggestive. If the atoms are compressible and are packed closely together in solids and liquids, may we not trace, through the alteration in bulk of substances during chemical change, the action of the chemical and cohesive affinities which hold the atoms together? May we not, with the help of this study interpret anew the mysterious symmetry of crystals? May we not correlate numerous properties in relation to one another and by means of the fundamental conception show the mutual dependence of all the properties of matter?

Perhaps the best method of indicating how such an idea can be of service is to enumerate the investigations which this particular hypothesis has already called into being, and the results to which they have led.

In the first place the hypothesis stimulated the study of the densities of solids and liquids, and thus led to the securing of decidedly convincing evidence that chemical affinity really exerts pressure in its action. This conclusion is based on the fact that the action of powerful affinity was found to be coincident with increase in density, other things being equal. Intimations of this effect are to be found in a note of Humphry Davy's, and in some later writings; but nobody had before taken account of its relation to the compressibility of the substances concerned.

A similar relationship was shown to hold in lesser degree with regard to the cohesion which holds together molecules of the same kind. Hence it appeared that non-volatile substances (which are firmly held together by cohesion) would be expected, other things being equal, to have great density, and great surface tension. Moreover, such substances (because already much compressed by great cohesion) should possess only slight compressibility. These conclusions likewise were verified by the study of fact.

The theory, since it involved the study of compressibility, led to the devising of a new and convenient method for determining this somewhat elusive property. With the help of this method the compressibilities of thirty-five elements were determined in Boylston Hall—only one or two having been known before. It was found that in the case of the solid elements the compressibility shows periodic fluctuation as the atomic weight increases, and that in general, with elements as with compounds, the

* So many partial, or inaccurate, statements of Prof. Richards's revolutionising theory have been printed of late, that the Editor of the *Graduates' Magazine* requested him to prepare the following article.

bulky volatile substances are the most easily compressible. This was new—neither the facts nor the explanation had been available before. The study of compressibility has since been taken up by Dr. Bridgman in the Jefferson Physical Laboratory, and he has made great progress in the study of the effect of high pressures.

Further, the theory suggested that if atoms are compressible, the uneven compression caused by differently applied chemical affinities might restrict the heat vibration supposed to exist within their elastic interiors. This restriction would lessen their heat-capacities (which are measured by the quantities of heat needed to cause a given change of temperature) and at the same time expel some heat vibration already present which could no longer be accommodated by the diminished heat capacity. Thus the theory predicted that when during a given reaction the heat-capacities of the substances concerned were diminished one would expect also to find an output of heat during this reaction in excess of that corresponding to the chemical work. This common-sense explanation of the puzzle involved in the idea of "bound energy" immediately stimulated investigation of the changes of heat-capacity of substances in relation to the corresponding changes in the heat evolved during chemical reaction, and also prompted the study of specific heats at very low temperatures. After the main relations had been qualitatively demonstrated at Harvard, the matter was taken up by Nernst in Berlin and later by others; and the qualitative predictions of the theory have been abundantly verified, even if the mathematical additions of some more recent investigators have not always been as effective as might be wished. The amplified idea has been called the "Third Law of Thermodynamics," and although by no means thoroughly worked out, it gives promise of fundamental importance.

Another suggestive application of the theory concerns the idea of the "asymmetric" or unsymmetrical carbon atom proposed by van't Hoff, which is the basis of so much of modern organic chemistry. The actually observed phenomena are exactly what one would expect if a compressible carbon atom were unequally compressed on four different sides by the four different affinities inherent in four other dissimilar atoms. This and other aspects of the theory were set forth in detail in the Faraday Lecture delivered in London two years ago.

The most recently published application of the hypothesis is its interpretation of crystal form. In a paper which has just appeared in the *Journal of the American Chemical Society*, various phenomena exhibited by crystals—such as their definite angles, the similarity of forms assumed by similar substances, and other details concerning their highly symmetrical shapes—are all accounted for according to the theory of compressible atoms in a fashion which seems (at least to the author) to be more satisfactory than any other thus far suggested.

Incidentally it may be noted that the theory is entirely consistent with the still more recent idea that the "atoms" themselves are composed of yet smaller corpuscles, although on the other hand I can see no reason why indivisible particles should not be compressible.

The applications of the theory to the interpretation of chemical phenomena and to the suggestion of new research are by no means exhausted. No significant objection to it has thus far been encountered; but even supposing that the idea should be supplanted in the future by something yet more satisfactory—and this is always a possibility in the progress of scientific thought—one would be inclined to say that the theory had already justified its existence. The saying of Scripture "By their fruits ye shall know them" applies in full force to theories as well as to persons, and in the short span of its existence the theory has been fruitful. It has "acquired merit" in the only way open to any such hypothesis, namely, by stimulating new experimentation, and thus leading to the discovery of facts and laws previously unknown.—*Harvard Graduate's Magazine*, xxi., No. 84.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

SPIRILLÆ OF RECURRENT FEVER.

As a sequel to the paper of M. Nicolle on the evolution of spirillæ in recurrent fever, Dr. Roux, director of the Pasteur Institute, has communicated to the Academy the observations of MM. Sergent and Folly concerning the momentary disappearance of the spirillæ between the feverish fits. If at this moment the blood of a subject attacked by the fever is injected into monkeys, the disease can in this way be inoculated in them. The inoculation of the disease is so much the longer when the blood injected has been procured at a moment nearer the first fit of fever. The authors of this paper conclude from these facts that it must be admitted that the spirillæ invisible with the microscope between the fits exist, however, in the blood in small quantities, and that they become more numerous when a fresh fit is coming on.

STAGE OF ACTIVATION OF THE PHENOMENON OF PARTHENOGENESIS.

M. Yves Delage has communicated to the Academy a paper of M. Bataillon, Professor at the Faculty of Science of Dijon, concerning the phenomenon of parthenogenesis. M. Delage establishes the fact that in this phenomenon there exists a primary stage of activation during which the egg that is made to undergo the biological reactions acts in exactly the same way as a fertilised egg. It resists the action of certain ferments, and M. Bataillon has been able to determine the precise moment when the activation is produced.

FOUNDATION OF NEW PRIZE OF PHYSIOLOGY.

A new prize of vegetable physiology has been founded at the Faculty of Science of Paris by M. Ruty de Lavison in memory of his son, a young physiologist killed in mountain excursion in Dauthiné. This prize has just been awarded for the first time to M. Roul Combe for his physiological researches on the colour of leaves and flowers.

THE LIFE OF THE INFINITESIMAL.

At the Institut Général Psychologique Dr. Comandon has just delivered a very interesting lecture on the life of the "infinitely small ones." In support of his theories, he presented the documentation supplied so usefully by cinematography in these matters. He showed first of all how different organs—the heart of a tortoise for example—isolated from the body can continue to live. He next spoke of the cellules of the blood, of vegetable cellules, of monocellular beings, such as the paramyces, of good and bad microbes, of the microbes of the intestines, of the trypanosomes of the malady of sleeping sickness, of the action of physical and chemical factors on the cellules of microbes, of the defence of the organism, and notably of phagocytosis, &c.

SCIENTIFIC JUBILEE OF GASTON BONNIER.

It was in 1889 that Prof. Gaston Bonnier founded the laboratory of vegetable biology at Fontainebleau and the *Revue Générale de Botanique*. On the occasion of the twenty-fifth anniversary of these creations the pupils and friends of this learned botanist intend to offer him, in this same laboratory at Fontainebleau, a volume of scientific memoirs written by the botanists who have collaborated in his laboratory work and in the above-mentioned Review.

A PERPETUAL ELECTRIC CURRENT.

A sensational communication has just been made to the Academy of Sciences: an electrical current, when once it is set on or primed can last indefinitely, or nearly so, without the cause that provoked the movement of electricity being renewed. It is through Prof. d'Arsonval that Prof. Kamerlingh Onnes has made known this extra-

ordinary fact to the learned assembly. It is by the utilisation of extremely low temperatures, which he has been the first to be able to realise, that the eminent physicist of Leyden arrived at this strange result. For a long time it has been known that, in cooling, metals oppose a gradually weaker and weaker resistance to the passage of the electric current. Ampère and then Clausius had even given out this idea that at the absolute zero, that is to say, in the absence of any thermal agitation, the electricity would pass without the least difficulty through any conductor made of pure metal. But the actual phenomena are more novel than they imagined. After having in his memorable experiments liquefied helium, Kamerlingh Onnes decided to pursue the experiments destined to make us better acquainted with the properties of bodies, as far as the lowest temperatures that it is possible to attain when it is boiled in an almost perfect vacuum. Conformably to his previsions he first saw the resistivity of metals take values still much lower at the temperature of solid hydrogen. But then appears a new phenomenon: at a determined temperature (4.19°C . absolute for mercury, 3.8°C . for tin, 6°C . for lead), the resistance falls suddenly to a value that it is impossible to measure or estimate. The metals then acquire a new property: they are *superconductors*. Then Kamerlingh Onnes asked himself this question: What becomes of the movement of the electricity in a bobbin or coil of such a metal closed on itself? With a very fine lead wire he constructed a helix of a thousand turns contained in a cubic centimetre. At the ordinary temperature its resistance was 736 ohms; in liquid helium this resistance fell to a value that was twenty milliard times weaker. By induction he obtains in this helix an electric current of more than half an ampère; now this current persists during several hours without any perceptible weakening in its force. As long as the temperature is not allowed to rise, the coil acts on the outside on the magnetic needle, and if, having previously soldered to the coil the conductors of a galvanometer, the continuity of the circuit is interrupted, the needle of the apparatus is seen to deviate suddenly. But everything immediately comes to a standstill, for the energy of the electric current is instantaneously run out in the resisting circuit of the compass. This singular phenomenon has evoked hopes that very soon may be realised, in a most simple fashion, one of the most cherished desires of some of the physicists of our days—the establishment of an intense magnetic field. Now this is where Nature was to reserve for the physicist a disappointing surprise; in a magnetic field of a certain intensity, which is so much the greater as the bobbin is more advanced in the state of super-conduction, the resistance rises, and we then possess only a metal of very high conductivity.

COAL IN MADAGASCAR.

A most interesting study of M. J. Giraud on the geology of Madagascar was presented before the Academy by M. Donville. He has noticed sandstones and felspathic slates of 200 metres thick with visible layers of coal in the region of Benombrà, of a formation analogous to that of the "Tillites" of the Transvaal and of India, and that might be classified with the Uralien. He has also noticed ferruginous sandstone and coal schists of 300 metres thick, and, lastly, in the upper Jurassic districts in the North of the Ambango, some "marnes" exceedingly interesting from an economical point of view, for they contain phosphated nodules of 45 to 50 per cent of tricalcic phosphate.

ELECTION OF A CORRESPONDENT.

The Academy at the end of the last sitting proceeded to elect a correspondent in the place of the late Sir David Gill. Three candidates were presented, Mr. F. W. Dyson, of the Greenwich Observatory; Mr. Campbell, of the Observatory of Lick; and Mr. H. Struve, of the Observatory of Potsdam. Mr. F. W. Dyson was elected by a majority of 30 out of 31 voters.

NICKEL STEELS.

A study concerning the properties of nickel steels had enabled M. Charles E. Guillaume to completely characterise for ordinary temperatures the singular anomaly of these alloys, and had led him to the discovery of the previous invar. As M. Le Chatelier explains, M. P. Chevenard was able at the steel-works of Imphy to extend these results to the interval of temperature included between 195° and 750° . The increasing number of applications of nickel steel gives great practical interest to the results of M. Chevenard. But besides this, these researches bring new arguments to the theory of these strange alloys, founded upon the hypothesis already confirmed by the discoveries of M. Pierre Weiss and his pupils, of the existence of the combination Fe_2Ni that govern the whole of the phenomenon. Thus, M. Chevenard was able to follow the irreversible properties of the ferro-nickels rich in iron, thanks to a cooling, which for the alloys nearest to Fe_2Ni has been pushed as far as the temperature of liquid hydrogen. The rôle of the combination Fe_2Ni has also been demonstrated. It is at this combination that the anomaly of ferro-nickels stop. Beyond that and as far as nickel the properties of the alloys follow the rule of mixtures.

CORRESPONDENCE.

PHOSPHORESCENCE OF SULPHUR.

To the Editor of the Chemical News.

SIR,—Some months ago in the *CHEMICAL NEWS* (cviii., 187, No. 2812) Mr. W. H. Watson gave an account of various experiments he had made on the "phosphorescence of sulphur."

As he quoted the names of Heumann, Baker, Moissan, and others who did investigate the matter, I cannot but persuade myself he overlooked some papers of mine respecting the same (*cf.* Léon Bloch, "Flamme de phosphorescence et flamme de combustion du soufre," *Comptes Rendus*, 1909, cxlviii., 148, 782; "Recherches sur les actions chimiques et l'unification par Carbotage," *Ann. de Chim. et de Phys.*, 1911, xxii., 460).

I would greatly be obliged to you if correction be made for this omission in the proper place. This I think can be provided for the more easily as Mr. Watson's observations and results are in all points a valuable confirmation of my views.—I am, &c.,

LÉON BLOCH, Dr. Phil.

Laboratoire d'Enseignement Physique à la Sorbonne,
Paris.

MISCELLANEOUS.

Geological Survey of the United States.—In order that the benefit of the Geological Survey's investigations may be given promptly to the interested public, the first results in its several fields are published in the form of short papers and preliminary reports and issued as separate chapters. Of these short reports those of economic interest will appear as "Contributions to Economic Geology," issued in the series of Survey Bulletins; those of more purely scientific interest, as "Shorter Contributions to General Geology," in the series of Professional Papers; and those on hydrology, as "Contributions to the Hydrology of the United States," in the series of Water-Supply Papers. The chapters in each of these classes will form an annual volume (the pagination and plate numbers running continuously throughout), and at the end of the year there will be issued for each series a volume title-page, table of contents, index, and possibly bibliographic lists. Librarians and others to whom all the parts are furnished should preserve them as they would preserve any other serial.

THE CHEMICAL NEWS.

VOL. CX., No. 2851.

A NOTE ON THE QUESTION OF ASSOCIATE ATOMS.

By F. H. LORING.

THE idea of associate atoms differing in atomic weight yet whole numbers (CHEM. NEWS, 1914, cix., 143, 169; see also p. 241) is one that should appeal to those who have a leaning towards the Prout hypothesis (*Annals of Philosophy*, 1815, vi., 321; 1816, vii., 111); at the same time, this idea should not be confused with a somewhat different atomic condition, namely, the variations in the atomic weights of elements derived from different geological sources.

A variation has been recently found in the case of lead from Ceylon thorite, which differs in atomic weight from lead derived from mineral rich in uranium (Soddy and Hyman, *Journ. Chem. Soc.*, May, 1914, p. 1402; abstracted in CHEM. NEWS, cix., 259). Other variations in the atomic weight of different leads have been observed (Maurice Curie, *Acad. Sciences*, Paris, June 8, 1914; *Comptes Rendus*, clviii., 1676; O. Hönlischmid and Mlle. St. Hrovitz, *Acad. Sciences*, Paris, June 13, 1914; *Comptes Rendus*, clviii., 1796; a note in *Science*, June 5, 1914, states that T. W. Richards and M. E. Lumbert have also carried out experiments on several lead-bearing minerals, and they report marked differences in atomic weight, and no spectroscopic difference; see *Journ. Am. Chem. Soc.* for July, 1914). Lead, however, in so many ways is an exceptional element, in particular being an end-product of radio-active change, that this discovery would seem to rank as possibly an isolated instance. Meteoric iron has the same atomic weight as terrestrial iron, and copper, silver, sodium, and chlorine always have the same atomic weights, though samples from different geological sources have been used in the determinations.

It would appear, therefore, that in all but radio-active cases (mixed end-products), the proportionate numbers and the magnitudes of associate atoms for a given element are constant, and it therefore becomes necessary to consider whether chlorine, to take an example, is actually made up of associates in the ratio 10 : 1, having respectively atomic weights 35 and 40, as the theory would indicate.

Turning to Sir J. J. Thomson's positive-ray experiments ("Rays of Positive Electricity," 1913, pp. 48-49), it might, however, be expected that there would be indications on the photographic plate of mercury lines corresponding with the mixed values 199 and 203, since the most probable atomic weight of mercury is close to the value 200.6 (C. W. Easley, *Journ. Am. Chem. Soc.*, xxxii., 1117; or CHEM. NEWS, 1910, cii., 231, 235), which calls for associates of the above magnitudes in respective proportions, say, 8 to 5.

The *m/e* values for mercury found by Thomson are given in column A in the following table, whilst the values necessary to agree with the associates are given in column B, assuming that the "199" atoms carry charges 1, 3, 5, and 7, and that the "203" atoms carry charges 2, 4, and 6:—

A.	B.
200	199.0
102	101.5
66.3	66.33
50.4	50.75
39.8	39.8
33.7	33.833
28.6	28.43

It will be seen from column B that, by assuming odd and even charges associated with the minimum and maximum atomic weight atoms respectively, the experimental figures given agree fairly well with theory, and that no serious discrepancy appears in this case. The experimental values are not perhaps close enough for a rigorous comparison.

Another method, though not experimental, should be of interest, especially in directing attention to certain definite values that might be more easily verified by some experiment,* if such values can be gauged beforehand—in particular, if the mercury values can be rendered probable by the coincidence of independent methods. One method consists in building up the inactive gases by the addition of experimentally-known values (or those deduced in conformity with experiments generally) of systematically related elements thus:—

$$\begin{aligned} \text{Be } 8.90 + (4 \times 7.5) + \text{H } 1.008 &= 39.908 = \text{Argon.} \\ \text{Ca } 40.02 + 7.5 + \text{Cl } 35.45 &= 82.97 \text{ or } 83 = \text{Krypton.} \\ \text{Zn } 65.33 + (4 \times 7.5) + \text{Cl } 35.45 &= 130.78 = \text{Xenon.} \\ \text{Sr } 87.56 + 7.5 + \text{Br } 79.90 &= 174.96 \text{ or } 175 = a. \\ \text{Cd } 112.43 + (4 \times 7.5) + \text{Br } 79.90 &= 222.33 = \text{Ra and Ac Em's.} \\ \text{Ag } 107.89 + 7.5 + \text{I } 126.92 &= 242.31 = b. \\ \text{Cu } 63.50 + (4 \times 7.5) + \text{I } 126.92 &= 220.42 = \text{Th emanation.} \end{aligned}$$

The values in particular, 8.90(?), 107.88, 222.33, and 220.428, have been previously deduced (CHEMICAL NEWS, 1913, cviii., 247; cix., 143; cix., 241); and they need not be discussed here. It is not suggested that the inactive gases are directly compounded in the above manner, although they may be analysable theoretically, in that their atomic weights are such as to include portions representing acid- and base-forming components answering to known elements.

a and *b* are hypothetical elements, presumably gaseous and inactive like the others. The latter (*b*) may have been a forerunner of uranium 1, i.e., its parent, but now extinct. Such an element would find a place in a right-hand extension of the Periodic Table of the radio-elements (CHEM. NEWS, cix., 241), if it emitted α -rays, as in the case of the known emanations.

It should be noted that the sequences, H—Cl—Br—I, Be—Zn—Cd—Cu, and Ca—Sr—Ag, not being wholly arbitrary, lend colour to the scheme.

Moreover, by another method, that of the associates, the above values are directly and indirectly supported, thus rendering the associate atoms (values) probable, as will be seen from the following comparisons:—

	Associates.	Elliptical method.	1914 I.C. values.	Summation method.
Zinc—	$64 \times 6 = 384$ $68 \times 3 = 204$ 9)588			
	65.333	65.34	65.37	65.33
Cadmium—	$111 \times 7 = 777$ $115 \times 4 = 460$ 11)1237			
	112.454	112.47	112.40	112.43
Mercury—	$199 \times 8 = 1592$ $203 \times 5 = 1015$ 13)2607			
	200.538	200.5	200.6	

* It is, of course, understood that the separation of chemically identical elements (isotopes) whose atoms differ in weight by an amount considerably less than that between the typical periodic homologues (Rb and Cs, for example) is a problem awaiting practical solution.

The elliptical method (CHEM. NEWS, xcix., 150) is not to be regarded as fully developed in respect of the higher values, but if one species of lead and mercury fall on a first ellipse of a third grouping, their values may be taken approximately as 207 and 200.5 respectively.

The following is a series which leaves little to be desired from the standpoint of regularity:—

Cu.	Zn.	Ga.	Ge.	As.	Se.	Br.
63×7	64×6	68×5	71×4	72×3	75×2	79×1
67×1	68×3	72×5	73×7	76×9	80×11	80×13
63.500	65.333	70.000	72.272	75.000	79.230	79.928
63.57	65.37	69.9	72.5	74.96	79.2	79.92

In the bottom row are given the International Committee values, which compare favourably with those by the method in question. As an alternative, gallium might have values 67 and 72, which would give differences between the top row numbers 1 : 3 : 4 = 1 : 3 : 4, but it is perhaps better to select such numbers as will best fit the experimental values.

The two remaining series of the same grouping are not quite so good, but there is no reason to suppose from them that the silver, cadmium, gold, and mercury values are not in order. Placing iodine as the 6th element in the series, it appears to have the composite make-up, thus:— $(126 \times 1 + 127 \times 12) / 13 = 126.923$. The lower multipliers or atom-numbers of this series may run 2, 4, 6, 8, 10, 12, 14.

In most cases the values are in singular agreement throughout the specification, neglecting a slight discrepancy in the second place of the decimals. It is probably expecting too much of such devices to hope for *absolute* agreement in the values obtained thereby, since probably such agreements, when they do occur, are accidental. This does not, of course, mean that they are without some significance.

A. D. Risteen ("Molecules and the Molecular Theory," 1895, pp. 159–161), discussing the Prout hypothesis, says:—" . . . But as we have never split an element up into its constituent hydrogen atoms (if, indeed, it contains such atoms!), there is no evidence that in such a case the 'law of conservation of weight' would still hold true. . . . On the other hand, whenever the law of conservation of weight would *not* be violated upon splitting a body up, the body in question is not an element, but a *compound*; and we can reasonably hope to effect its separation into two or more simpler bodies. This hypothesis explains both the existence of 'elements' and the slight deviation from integral values that we find in their atomic weights."

Sir E. Rutherford (*Phil. Mag.*, 1914, xxvii., p. 488) regards the hydrogen atom as possibly the *positive* electron, and $4H = He$, in which the slight difference in the equality of the equation due to the hydrogen fraction, may be accounted for on the Lorentz theory, according to which the mass of H may be taken as electromagnetic, this mass suffering some slight change when a number of fields react in giving rise to a stable configuration. Rutherford inclines to the view that most of the elements are made up of helium units—a theory which has been regarded as possible for some years. Radio-activity is a proof positive that, to some extent at least, such is the case. The idea of associate atoms is in harmony with these views when rightly interpreted.

Errata and Addenda.—In a previous communication (CHEM. NEWS, cix., 241), a few typographical slips occurred, which should be corrected. On bottom of p. 241, insert Roman numerals respectively I. and II. after each Th-end. Similarly, insert I. after Ac-end, and the sub-number 5 after 211 in line below. It is, of course, understood that the Roman numerals do not represent valencies or group numbers. It was perhaps a mistake to use existing nomenclature in a newly-intended sense, but the choice of indicating signs is rather limited, since all kinds of signs have been appropriated for one purpose or another. On

page 242, towards the top, Hevesey should read Hevesy. Towards the bottom of the same page in the paragraph beginning with "Commenting," instead of "their energy" read: their excess of energy. In the next paragraph delete the word "backward." In the foot note substitute 4 for 5 to make the series of figures regular.

Referring to the percentage figures, they were taken from current papers, and they have only a relative significance, besides being only strictly comparable when members of the same family are taken. Also, the arrows representing ray—or, in a few cases, apparently rayless—changes, should be considered as *multiple*, when taking into account the proportionate numbers of associate atoms in process of change.

A REGULARITY BETWEEN MOLECULAR HEAT OF COMBUSTION AND ITS BEARING ON THE CONSTITUTION OF THE HYDROCARBONS.

By GERVAISE LE BAS, B.Sc.

SOME years ago I made a communication in the form of a letter to the CHEMICAL NEWS on the above subject, which was adversely criticised by Mr. S. Redgrove, B.Sc., and which I did not answer at the time. Since then a number of explanations of molecular heats of combustion, of varying degrees of ingenuity, have been offered. On looking over this old work of mine I still think that, with necessary alterations, it is worth bringing to light.

In the present paper I propose dealing solely with the hydrocarbons, because the light thrown on their chemical relationships by the heat of combustion is sufficient to justify their separate treatment.

The data are chiefly those due to Thomsen and Stohmann (for the aromatic and hydro-aromatic compounds), but one or two are due to Berthelot.

The molecular heats of combustion of chemical compounds may be considered to be the balance of the heats produced by the union of the separated atoms with oxygen over the amounts absorbed by their dissociation. Whatever may be the actual mechanism of the process, the results depend solely on the initial and final states, and the hydrocarbons represent so much potential energy relative to their oxidised atoms which is liberated by the process of combustion.

The heat of dissociation is no doubt an additive function of the composition, just as are the unknown absolute heats of combustion of all the atoms. The observed heats of combustion, which represent the differences between the two processes, are thus likely to be additive also.

The final products in this instance are gaseous CO_2 and liquid H_2O . If we wish to consider the products under similar physical conditions, it will be necessary to subtract 9 calories from the results for each *gram-molecule* of water condensed, but it is evident that if we do not, the additive nature of the relation will not be prejudiced. The correction for constant pressure, where necessary, is small.

Any additive relations which may be observed after discussion of the results are therefore significant, and the constants obtained represent respectively the absolute heat of combustion of C minus the heat absorbed on separation from the molecular complex, and the absolute heat of combustion of H minus the heat absorbed on separation from carbon. This is essentially the principle involved in the usual process of referring the combustion values of compounds to the heats liberated when so many *gram-molecules* of carbon in the form of diamond are burned, and when so many *gram-molecules* of hydrogen are consumed. In neither case do we consider the amount of heat absorbed when the four valency links of C are broken in the complicated molecule present in the diamond, nor the amount absorbed when the link $H-H$ is broken. The

numbers (C) = 94.3 K and (H) = 67.5 K are universally regarded as the effective heat values of the combined carbon and hydrogen atoms present in their respective molecules. Similarly, the numbers (C) = 106.0 and (H) = 26.5, which are brought out by the additive relation to be immediately indicated, are considered to represent the effective combustion values of carbon and hydrogen in the respective gaseous paraffins. It will be unnecessary in the comparative study of the hydrocarbons which is now being undertaken, to consider the amounts of heat absorbed in the rupture of the bonds (C—C), (H—C). No special stress is laid on the particular values of the constants found. The important point is the use which can be made of them to determine the constitutions of a number of hydrocarbons, saturated and unsaturated. The regularity starts with the almost constant differences for CH₂, viz., 158.4 K. This represents the effective combustion value of methylene. We also find that the M.H.C. are proportional to a series of numbers 8, 14, 20, . . . for the simplest paraffins, and the constant is obviously the combustion value of (H) under the circumstances.

The Gaseous Paraffins.

C_nH_{2n+2}	M.H.C.	Δ	n	$\frac{M.H.C.}{n} = (H)$
Methane, CH ₄ . . .	211.9	158.5	8	26.49
Ethane, C ₂ H ₆ . . .	370.4	158.8	14	26.53
Propane, C ₃ H ₈ . . .	529.2	158.0	20	26.46
Butane, C ₄ H ₁₀ . . .	687.2		26	26.43
Mean values . . .		158.4		26.48

The value for (H) is thus 26.48, and for (C) 211.9—105.9 = 106.0.

These numbers stand to each other in the relation 1 : 4.

Thomsen's formula is—

$$C_aH_{2b} = aA + bB + \gamma C + zD + 0.580.$$

where—

A = P—2U (the effective combustion value of C), and—

B = 2Q + U—2S—0.290 (the effective combustion value of H). (See Nernst's "Theoretical Chemistry," p. 276).

Thus the general argument previously given is here set forth symbolically. The additive principle is recognised.

Thomsen's constants are A = 106.17, B = 52.53. The first constant refers to (C), the second to 2(H). Thomsen's value for (H) is thus 26.26. These numbers are similar to those here given (C) = 106.0, (H) = 26.48. The 4:1 rule is so simple and easy of application that its use for our purpose is more advantageous than Thomsen's method, and it seems to have some theoretical significance.

The Liquid Paraffins.

C_nH_{2n+2}	M.H.C.	Δ	n	$\frac{M.H.C.}{n} = (H)$
Heptane, C ₇ H ₁₆ (S) . . .	1152.0	161.0	44	26.20
Octane, C ₈ H ₁₈ (S) . . .	1313.0	(2 × 155.5)	50	26.26
Decane, C ₁₀ H ₂₂ (B) . . .	1624.0		62	26.20
Mean, 6 × 26.2 = 157.3.				

The Solid Paraffins.

Hexadecane, C ₁₆ H ₃₄ (B) . . .	2558.6	4 × 155.9	98	26.10
Eicosane, C ₂₀ H ₄₂ (B) . . .	3182.5	6 × 26.0	122	26.09
Mean, 6 × 26.0 = 156.0.				

The constants are smaller for the solid and liquid substances, as we might expect, but it is noteworthy that, in spite of the changes of state, the 4:1 rule still holds. This shows that the changes in the heat values due to change of state affect every C and every H atom proportionately.

So far we have dealt with saturated substances, but the rule may be applied to unsaturated substances also. Thomsen worked out formulæ for unsaturated substances, and found additional constants for them.

C = 2U—V = 15.465, increment for every double bond.

D = 3U—W = 43.922, increment for every triple bond.

The Gaseous Olefins.

C_nH_{2n} = .	M.H.C.	n	$n \times 26.48$	Δ for =
Ethylene, CH ₂ :CH ₂ . . .	333.3	12	317.6	+15.7
Propylene, CH ₃ .CH:CH ₂ . . .	492.7	18	476.6	+16.1
Isobutylene, C ₂ H ₅ .CH:CH ₂ . . .	650.6	24	635.5	+15.1
Diallyl, —CH ₂ :CH.(CH ₂) ₂ CH:CH ₂	932.8	34	900.3	2 × 16.2
Mean value . . .				= + 15.8

The Gaseous Acetylenes.

Acetylene, CH:CH . . .	310.0	10	264.8	≡ + 45.2
CH ₃ .C:CH . . .	467.5	16	423.7	+43.8
Dipropargyl, C ₆ H ₆ ≡ ₂ . . .	882.9	30	794.4	2 × 44.2
Mean value . . .				≡ + 44.3

The numbers | = | = +15.8, |≡| = +44.3 resemble Thomsen's constants, C = 15.46 and D = 43.92.

That these features of the olefins and acetylenes represent some real property of matter is shown by similar corrections necessary for other physical measurements when the respective physical properties are considered.

Thus, for *Refractive Power* (Brühl),—

$$| = | + 1.836, | \equiv | + 2.27,$$

for *Magnetic Rotatory Power* (Perkin),—

$$| = | + 1.1 \text{ approx. } | \equiv | + 1.750,$$

and for *Molecular Volumes* I have shown that, at the melting-points of the complex olefins and acetylenes,—

$$| = | - 2.62, | \equiv | - 3.26.$$

The — sign, indicating a decrease in volume, is in the right direction, and corresponds to an exaltation of the other properties (*Phil. Mag.*, 1908, [6], xvi., 62).

This feature does not show itself at the boiling-point for reasons which need not here be considered, but which are dealt with elsewhere.

These results imply that the substances, which are unsaturated in a material sense, are also unsaturated as regards energy content; that is, possess free energy, or energy only loosely held.

The increments in M.H.C., which have been observed, show that less energy is necessary to split up an olefin or acetylene hydrocarbon, relatively speaking, than to split up a saturated paraffin by a constant amount. This is due to an inherent weakness of the attachments in the combinations, —CH:CH₂ and —C:CH, and is probably perfectly compatible with the existence of loosely held energy or residual affinity, which gives rise to strain in the molecule. This instability of olefin and acetylenic compounds is a fact repeatedly observed in ordinary chemical experience.

(To be continued).

Saponification of Ether Salts and Amides by Concentrated Sulphuric Acid. — J. Bougault. — In the saponification of ether salts and amides by sulphuric acid the latter only intervenes to form an addition product, and it is the water in which the reaction takes place which causes the saponification and liberates ammonia and alcohol. — *Comptes Rendus*, clviii., No. 20.

THE PRESENT STATE OF THE CYANAMIDE INDUSTRY.*

By E. J. PRANKE.

(Concluded from p. 22).

Dust.

ATTENTION has often been called to the dustiness of the powdered cyanamide, and to its caustic action on the skin and mucous membranes. In some fertiliser factories loosely constructed elevators and mixing machines, and open screens permit the escape of the fine material, which settles on the exposed parts of the labourer's body. If then the labourer fails to wash the dust off at the conclusion of the day's work, the lime compounds will absorb moisture and probably some of the natural oils from the skin, and cause some irritation. If, however, the labourer will rub any kind of oil or grease on the exposed parts of his body before he commences work, and will use oil or grease again at the conclusion of the day's work, he will find that the dust will not burn during the day, and is very easily wiped off when he is through with his work. Of course the dust must be removed from the skin at least once a day. Labourers who work in the factories where cyanamide is made never have skin irritation. They take the simple precautions that have just been described.

It is a peculiar fact that when alcohol is taken into the body after one has breathed cyanamide dust, there follows within a few minutes a reaction colloquially known as a "flush." This is characterised by an increased flow of blood to the skin, of the upper part of the body, deepening its colour, and giving a suggestion of swelling. The subject also has a feeling of oppression in his breathing. In no case has anyone ever been known to suffer harm from a "flush," but only temporary discomfort, the degree depending upon the amount of alcohol imbibed. The effects usually pass away within an hour after taking the alcohol. Moreover, alcohol is the only known cause of this effect of breathing the dust. Total abstainers never experience the "flush."

In the better equipped fertiliser factories, the machinery is enclosed in such a way that practically no dust escapes. As soon as the cyanamide becomes a part of the mixture the dust is effectively laid by the large excess of other materials, many of which are naturally damp.

Granulated Cyanamide.

During the past year there was placed on the market in this country a granulated cyanamide, which is practically free from dust. This material is made by pressing damp cyanamide into briquettes, which after hardening are ground, and the product screened to sizes between 15- and 60-mesh sieves. On the basis of the original estimated cost of granulating, this improved product was sold at a premium of 7 to 8 per cent over the price of the powdered material. Actual operation records show, however, that the cost of granulating is more than double this amount. When the price of granulated cyanamide was advanced sufficient to cover the manufacturing expense of producing it, the demand practically ceased. Consumers apparently will not pay a premium of 15 per cent for dustless material.

Agricultural Use and Value.

Perhaps the most important question that can be asked about cyanamide is: What is its fertilising value? Does it give to the farmer year after year a consistent profit on his investment that compares favourably with the profit on an equal expenditure for some other material?

One way to answer the question is to fertilise one-third of a field in the ordinary way with a properly compounded commercial cyanamide mixture, fertilise another one-third with some other standard mixture of equivalent analysis,

and omit fertilisers from the remaining one-third. The answer given by such an experiment usually is that cyanamide may be profitably substituted for an equivalent amount of nitrogen in other standard forms.

Unfortunately, a commercial fertiliser mixture is usually regarded by the orthodox scientific investigator as too complex to fit into the logical scheme of his fertiliser test-plats. He wants to test the unmixed cyanamide, and he usually wants to use it in quantities far more generous than any that the farmer would ever think of applying. The results of his small plat or pot experiments often do not agree with the farmer's field experience. There are four principal reasons for the difference:—(1) Excessive applications of any of the common inorganic ammoniates may cause injury to the plants, and cyanamide is somewhat more active in this respect than the others; (2) cyanamide behaves agriculturally like an organic ammoniate, and is not strictly comparable with the other inorganic ammoniates; (3) certain mixtures of two or more different kinds of nitrogen usually give a larger yield than the same quantity of nitrogen in one form alone; and (4) the cyanamide in commercial mixtures is transformed by interaction with phosphates, and loses its identity.

The farmer's use of fertilisers in general is guided solely by the profits derived therefrom. He is continually seeking to learn in what way and in what amounts he shall apply his fertilisers so as to derive a maximum profit. The broad result of this general searching for the best ways is the formation of certain standards of fertiliser practice. These standards are in actual operation on the farms where the most money is being made. For the great staple crops, wheat, oats, corn, hay, and cotton, the application of nitrogen gives increasing profits up to the point where about 200 lbs. of cyanamide or the equivalent thereof in other forms is applied per acre. Above this amount of nitrogen, additional applications will produce additional yields, but the value of the extra yield will not, except in the case of very good soils, exceed the extra cost that it took to produce it. Now if cyanamide produces satisfactory results with this maximum economical application, what reasonable objection can there be if it does not produce satisfactory results when used in quantities from two to four times as large? Yet objections have been made against it, based upon each excessive applications in small plat or pot experiments.

The effect of excessive applications of unmixed cyanamide is more evident on acid light sandy soils than on any others. This is probably due to two causes:—First, the absorbing power of such soils is low, since the coarse soil particles do not present the large amount of surface that is offered by the much finer particles in the loam and clay soils; and second, bacteria are notably deficient in such soils. The remedies for this situation, if it is necessary to use the unmixed cyanamide, are two:—First, not more than 250 lbs. of cyanamide per acre should be applied, either spread broadcast and worked well into the soil, or if applied in rows, put down in two applications; second, the acid soil conditions should be removed and the bacterial condition improved by the use of sufficient lime, before fertilising or as a part of the fertiliser. In other words, the object is to avoid too high a concentration of cyanamide in any one portion of soil, and to favour the conversion of the cyanamide to other forms of nitrogen.

Practically, there is no more necessity for applying excessive quantities of one kind of ammoniate, than there is for feeding an animal an excessive amount of one kind of food. There are stock-foods, green clover, for instance, that may kill an animal if fed to excess at one time, and there are many articles of human food that will cause serious illness if eaten to excess, but that is no objection to their use in normal economical quantities. When it is necessary to apply large quantities of nitrogen to certain crops, such as truck crops, potatoes, fancy tobacco, &c., it is customary and desirable to derive the nitrogen from several sources, and not from one only. The use of 200 lbs. of cyanamide per acre in rows, or 300 lbs.

* Presented before the Nashville, Tenn., Section of the A. C. S., February 20, 1914. From the *Journal of Industrial and Engineering Chemistry*, vi., No 5.

broadcast, would be economical and satisfactory on such crops, but additional nitrogen should be derived from other sources.

Experience has taught the practical fertiliser manufacturer that a mixture of different forms of nitrogen, properly chosen, almost invariably gives better results than an equivalent amount of nitrogen in a single form. It is well known that different ammoniates yield their nitrogen to the plant in an available form at much different rates, depending upon the nature of the fertiliser, soil conditions, climate, &c. Thus, with respect to the rapidity with which they yield available nitrogen the common ammoniates may be arranged in about the following order, beginning with the most rapid :—

1. Sodium Nitrate.
2. Ammonium Sulphate.
3. Cyanamide, Cottonseed Meal, Castor Pomace.
4. Dried Blood, Dried Fish, Tankage.
5. Steamed Bone, Ground Raw Bone.

When applied at the usual rate the quick-acting ammoniates supply an abundance of nitrogen in the early stages of growth, but little or none in the last stages. The slow-acting ammoniates do not supply an adequate amount of nitrogen in the early stages, while those of medium activity are ineffective both in the beginning and in the final stages of growth. It is obvious that a mixture of ammoniates that will furnish a uniform stream of available nitrogen from the beginning of growth to maturity will produce better results than a single ammoniate of equal nitrogen content that furnishes an over-supply of available nitrogen at one time and is deficient at other times.

The above applies only to the economical fertilising of plants, where just enough nitrogen is added to supply the plants' requirements. Where there is a great excess of nitrogen applied, there is almost certain to be a sufficient supply to meet the plants' requirements at all stages of growth. Even the most active form of nitrogen would last longer than the period of growth of the plant if enough were applied at the start, but such applications would not be economical on account of unavoidable losses.

The common practice, therefore, of estimating the relative value of different ammoniates by measuring their results when applied to a common task is not strictly accurate. Fertiliser materials have as much individuality and are as different in their functions as are different kinds of building material, or different breeds of horses, or different kinds of clothing. Some excel in one respect, and others in another respect. Cyanamide, for instance, may take the place of the organic ammoniates of intermediate activity, because the nitrogen in these materials becomes available at about the same rate, and under the same conditions as cyanamide nitrogen. It cannot, however, act as successfully as sodium nitrate, when the object is to produce forced growth, because cyanamide is not in the class of forcing ammoniates. The fact that a draft horse cannot travel a mile in three minutes argues very little as to his ability as a draft horse.

The great majority of the reports on the fertilising value of cyanamide as found in the literature, therefore, have little significance for the American manufacturer of fertilisers. The question to which he wants an answer has been very little touched upon. This is: "What is the effect of putting cyanamide in place of one or more of the other ammoniates, especially the expensive organic ammoniates, in fertiliser mixtures?" From observation of practical mixtures, however, the answer is, that cyanamide is a successful substitute for the medium to slow-acting organic ammoniates.

Another reason why results with the pure cyanamide may not hold for the actual cyanamide mixtures sold in America is found in the fact that practically all the cyanamide used in this country is sold to fertiliser manufacturers, and practically all of it is used in acid phosphate mixtures. A very little is used in basic slag mixtures, and a small amount in other ways.

When cyanamide is mixed with acid phosphate there is an immediate reaction, resulting in the complete breaking down of the calcium cyanamide. The calcium is fixed as mono- and di-calcium phosphates—the nitrogen is hydrolysed to urea. Urea, from the fertiliser standpoint, seems to be the ideal form of organic nitrogen. It is extremely soluble, can be directly assimilated by plants, but if not immediately absorbed, reacts with the soil particles, and becomes fixed as rather insoluble double ammonium salts, that do not easily wash out of the soil. By this chemical reaction, therefore, the identity of the original cyanamide is destroyed, and a new set of properties is established, namely, the properties of a mixture of urea nitrogen with mono- and di-calcium phosphates. This is what the American farmer gets when he buys a commercial cyanamide mixture made with acid phosphate as the source of phosphoric acid. The practical results from such mixtures are, as one would expect, entirely satisfactory.

Basic slag mixtures are used to some extent in the States along the Atlantic Coast. On acid sandy soils basic slag is probably somewhat more effective than acid phosphate, probably owing, in a large measure, to the action of the lime in neutralising soil acids, and permitting the restoration of bacteria in proper numbers. Slag contains from 15 to 18 per cent iron, and about 5 per cent manganese, both of which are powerful catalysers of cyanamide to the urea form. The practical experience with these mixtures seems to be entirely satisfactory.

We see, therefore, that practically there is no need of applying more than 200 lbs. of unmixed cyanamide per acre at one time on the staple crops, or 300 lbs. per acre on truck crops. If more nitrogen than this is needed, it should be derived from additional sources. The great majority of the reports found in the literature on cyanamide are practically worthless because the experiments were made with excessive quantities. The only thoroughly satisfactory and valuable test from the farmer's point of view, is one that conforms to the economic requirements that govern the use of any fertiliser, and is made under practical farm conditions. Since practically all the cyanamide sold in this country reaches the farmer as a mixture of urea nitrogen and mono- and di-calcium phosphates, it is only necessary to know what results are being obtained with such mixtures. The reports are almost unanimously favourable.

Mixing with Acid Phosphate.

The statement can be found in many places in the literature that "Cyanamide must not be mixed with acid phosphate, since thereby the available phosphoric acid is converted to the insoluble form." On charts showing incompatible mixtures of fertiliser materials, the mixtures of cyanamide and acid phosphate are always indicated as not practical. Nevertheless, as was said above, practically all of the cyanamide sold in this country is used in mixtures containing acid phosphate.

In the average phosphate most of the phosphoric acid is in the water-soluble condition (as free phosphoric acid and mono-calcium phosphate), a small amount is present as di-calcium phosphate, not soluble in water but soluble in ammonium citrate solution, and a small amount is present as phosphates insoluble in ammonium citrate solution. When a small amount of cyanamide or other active lime compound is added to acid phosphate, there is an immediate reaction between the lime and the water-soluble phosphoric acid, resulting in a change of the latter to the citrate-soluble form. Both of these forms have about the same agricultural value, and both have the same commercial value. When a large amount of cyanamide is added to acid phosphate, however, there is a more complete neutralisation, resulting in the formation of forms containing more lime than di-calcium phosphate contains, and these forms are not soluble in citrate solution; hence, they have no commercial value.

Now it happens that the experiments reported in the literature were mostly made with large quantities of cyan-

amide, hence the results were unfavourable to such mixtures. On closer investigation of this problem, however, paying attention to the quantitative factors involved, it was found that as the quantity of cyanamide used with respect to the acid phosphate decreased, the loss of available phosphoric acid decreased. When the quantity of cyanamide is as small as 60 to 80 lbs. of cyanamide to a ton of average complete mixture containing approximately 1000 lbs. of acid phosphate, the loss of available phosphoric acid is not appreciable. *It is at this rate that most of the cyanamide sold in this country is used in commercial fertilisers.* In some cases as much as 150 lbs. is successfully used. The acid phosphate must be dry in this case, and as much bulky organic matter as possible used.

Mixtures with Ammonium Sulphate.

It has also been said that cyanamide must not by any means be mixed with ammonium sulphate, since the lime in the former will drive out free ammonia from the ammonium sulphate. This is true if we consider a simple mixture of only the two substances. It is also true for mixtures of cyanamide, ammonium sulphate, and acid phosphate, if large quantities of cyanamide are used. If, however, we pay attention to the quantitative factors again, we find that when there are not more than 150 lbs. of cyanamide present along with ammonium sulphate and 1000 lbs. of acid phosphate, there will be no escape of ammonia from the mixture. The ammonia set free by the lime is caught by the acid phosphate, and fixed as ammonium phosphates. Since the use of acid phosphate with cyanamide imposes a limit of less than 150 lbs. of cyanamide per ton of mixture it is not possible to reach a large enough quantity of cyanamide in such mixtures to cause a loss of ammonia. Hence, in all commercial acid phosphate mixtures, made with due regard to the necessity of keeping the phosphoric acid available, there is no possibility of liberation of free ammonia.

Special Advantages.

It may not be amiss here to name the special advantages that commend the use of cyanamide to the fertiliser manufacturer:—(1) It is a low-priced material; (2) it has a powerful drying-out action on damp materials used in mixtures; (3) it removes free acids from the acid phosphate, thus preventing rotting of bags, and loss of nitric acid from sodium nitrate in the mixture; (4) it adds agriculturally available lime to the mixture; and (5) it can successfully replace part or all of the more expensive organic materials in a fertiliser.

Summary.

1. The cost of food products in the United States has increased about twice as fast as the cost of other commodities, and about twice as fast as the general cost of living throughout the world. This tendency can be offset by an increased crop production, which will lower the price of food products, and hence the cost of living. Fertilisers are the most important single factor in increasing the crop production.

2. Nitrogen is the most expensive and agriculturally most necessary element in commercial fertilisers. A general reduction in the cost of the latter must come through increased production of nitrogen at lower cost. The cyanamide process is probably the cheapest known source of fertiliser nitrogen.

3. The rapid successful development of the economically important cyanamide industry has been full of difficulties, practically all of which has been overcome or minimised by paying attention to the quantitative factors involved.

4. The greatest common error in the experimental testing of cyanamide has been in the use of excessive quantities. When used in normal agricultural quantities, the results are entirely satisfactory.

5. All difficulties from the farmer's standpoint are

removed by the complete reaction of the cyanamide with acid phosphate in commercial mixtures. Such mixtures consume practically all of the American output of cyanamide.

6. Cyanamide has several special advantages as an ingredient in mixed fertilisers.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

THE ORIGIN OF PETROLS.

M. de Launay presents to the Academy a study of M. Jean Chantard on the origin of petroleum. M. Chantard, who has personally studied a large number of petroliferous beds all over the world, arrives at the conclusion that petroleum is related to the intermittent retrogressions of the sea; that is to say, that it was necessary for the sea to recede to form lagoons. If, on the contrary, the retrogression is continual, only salt deposits are formed. The new idea put forward by M. Chantard is that the intermittent marine retrogression must have coincided with sudden variations in the conditions of the deposit of organic matters.

VACCINATION OF RABIES BY VENOMS.

An extremely interesting communication has been made to the Academy of Sciences by M. Edmond Perrier, director of the Natural History Museum, in the name of M^{me}. Phisalix. The fine researches of M^{me}. Phisalix on the venoms of batracians and serpents are well known. A series of new and quite recent researches have shown M^{me}. Phisalix that the cutaneous and mucous secretions of batracians associated with the venom of the viper could vaccinate animals against experimental rabies. It is a most unexpected discovery and exceedingly interesting from a biological point of view. This learned naturalist already remarked some time ago that the mucous secretion of batracians was capable of giving animals immunity not only against its own action, but also against the venom of the aspic viper. The venoms of batracians and serpents having paralyzing properties M^{me}. Phisalix thought of making use of these venomous juices to try and confer immunity on animals against the virus of rabies, which also acts on the nervous centres by paralyzing them. Several rabbits were experimented upon. M^{me}. Phisalix injected into their veins some mucus of the salamander at intervals of several days. Some days after they were inoculated with a considerable dose, about 10 mgrms. of venom of the aspic viper, which dose was more than twice enough to be mortal for the witness rabbits. Six days after this last trial the rabbits thus treated were trepanned and some fixed rabic virus was injected into their meninges. Now, whereas no rabbit generally is proof against rabies in these conditions, the rabbits vaccinated with the associated venoms of the salamander and of the aspic continued in perfectly good health. The third that had been inoculated with the rabies fifteen days after having received the viper venom died rapidly. The length of the immunity conferred by the venoms of salamanders and vipers is then not very long. M^{me}. Phisalix has made other experiments to determine the duration of this immunisation. She has observed that although the effects of the vaccination persists generally two, three, and sometimes six weeks, the immunisation disappears after two months. M^{me}. Phisalix has likewise searched to see if of the two venoms there was one that had a preponderant action. Some rabbits were inoculated only with the venom of the salamander, others with only the venom of the aspic viper. None of them were proof against the injection of fixed rabic virus into the brain. Their resistance, however, seemed to be slightly increased. Yet the two associated venoms created a veritable immunity, an effective vaccination, but, unfortunately, only of a short duration against rabies.

LEVELLING OF THE EARTH.

At the last international geodesic conference, M. Charles Lallemand, director of the service for the general levelling of France, gave five reports, all exceedingly interesting, which he has just presented to the Academy of Sciences. During the period from 1900 to 1912 the levellings of precision were increased for the whole Earth by 33,000 kilometres, and at the present time the network of levellings of precision covering our globe amounts to 320,000 kilometres, or about eight times round the Earth. M. Charles Lallemand indicated, on the other hand, to the learned assembly the International Geodesic Conference had unanimously adopted his proposition in view of the creation of a new category of levellings of high precision, double that required up till now. The limit of error will be brought down for these levellings to a millimetre of probable accidental error per kilometre and to a tenth of a millimetre of probable systematic error. These lines of levellings take into account the improvements that have been brought about in the construction of instruments as well as the improvement of the method during the last thirty years.

THE EVOLUTION OF MATTER.

A learned German mathematician and physicist, Herr Einstein, has shown, according to mathematical deductions and from an application of the principle of relativity, that a body that radiates light loses its mass. In a paper presented by M. Deslandres, Director of the Observatory of Meudon, Dr. Gustave Le Bon, informs the Academy that he had already made that observation which was published in his book on the evolution of matter. It was after his experiments on cathodic rays that Dr. Gustave Le Bon had formulated his hypothesis that bodies radiating light lost their volume. But this loss of mass is very slight. Thus the loss of the sun's mass cannot be appreciated by measure, in spite of the observations to which it has been subjected for more than two thousand years.

THE ULTRA VIOLET RAYS AND SERUMS.

The effects of the ultra-violet rays on serums have just lately been studied by MM. Pierre Delbet and Beaudy in a paper presented before the Academy of Sciences by Prof. Dastre. The hemolytic properties of serums due to the combination of alexine and the sensibilisator are considerably altered and deteriorated by the ultra-violet rays. The alexine is destroyed by these radiations and the sensibilisator is modified. The physico-chemical properties of the serums are, on the contrary, not altered by the ultra-violet rays.

A NEW ALKALOID.

M. Georges Tanret has just discovered a new alkaloid that he has taken from the grains of a leguminous plant, the *Galega officinalis*. In a work communicated to the Academy by Prof. Dastre, M. Tanret has studied the physiological effects of this alkaloid. Numerous accidents have happened in the flocks feeding in the meadows in which this leguminous plant has been found. The galegine is a paralyser of the nervous system.

British Pharmacopœia, 1914.—At its meeting on July 13, the Executive Committee of the General Medical Council formally adopted as "The British Pharmacopœia, 1914," the completed draft submitted by the Pharmacopœia Committee. It was resolved that copies, in advance of publication, should be made accessible to the public for inspection at the offices of the Council in London, Edinburgh, and Dublin on Monday, August 10, at 10 a.m., and thereafter from 10 a.m. to 4 p.m., and that a copy for review should on the same day be placed in the hands of the Editor of each of the Medical and Pharmaceutical Journals on the Registrar's list. The official publication of the new British Pharmacopœia will be made by notice in the *Gazette* on Friday, October 9, on which day copies will be on sale by the publishers, Messrs. Constable and Co., Ltd., 10, Orange Street, Leicester Square, W.C.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 25, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"Spectrum of Elementary Silicon." By Sir W. CROOKES, O.M., Pres. R.S.

The accurate tabulation of the wave-lengths of lines in the silicon spark spectrum is of importance in physical astronomy, as several stars, especially of the *Orion* type, have spectrum lines corresponding to some of silicon. Few elements have had so much attention directed to their spectra as silicon, and scarcely any element has shown such diverse results between recorded observations by different observers.

I have tried in vain for years to get pieces of fused silicon in an approximate degree of purity. Lately the Carborundum Co. at Niagara Falls sent me three samples giving an analysis of 99.56, 99.86, and 99.98 per cent of silicon, the impurities being titanium, iron, and aluminium. This material has been used in the present research.

Fused silicon, used as electrodes with a strong induction spark, gives some trouble owing to a coating of oxide forming almost at once. The surface of the electrode now shows a curious *pitted* appearance, and the spark becomes much less luminous.

The instruments used for photographing and measuring the lines are those described in my paper on the "Ultra-violet Spectrum of Radium." Pure iron was used as a standard when practicable.

There are two lines in the orange-red part of the silicon spectrum which are extremely faint and hazy in appearance, requiring several hours' exposure with sensitive isochromatic films with the 5-prism quartz train. I therefore used for these lines an instrument designed some years ago for recording eye observations with the spectrograph. The apparatus takes the place of the camera in the 5 prism spectrograph.

The paper now submitted gives a complete list of silicon lines from λ 2124.163 in the ultra-violet to λ 6371.032 in the extreme red, with some remarks referring to missing or doubtful lines.

"Note on Mr. Mallock's Observations on Intermittent Vision." By Prof. S. P. THOMSON, F.R.S.

In his paper of December, 1913, on "Intermittent Vision," Mr. Mallock discussed the phenomena observed when a rotating disk of twelve black sectors painted on a white ground is viewed while a slight mechanical shock is given to the body or head. He concluded that a mechanical acceleration imparted thus to the nerve structures on which vision depends produces a momentary periodic paralysis. The author, repeating Mr. Mallock's experiments, finds that effects of precisely the same kind appear when on viewing the rotating sector disk in a mirror mounted elastically on a support, slight mechanical shocks are given to the mirror instead of to the observer. He therefore attributes the effects, both in Mr. Mallock's original experiments and in his own, to momentary minute displacements of the image on the retina, stimulating rods and cones which are relatively unfatigued and which therefore are momentarily of greater sensitiveness.

"Attempts to Produce the Rare Gases by Electric Discharge." By T. R. MERTON.

An investigation has been made of the apparent production of neon and helium by electric discharges in vacuum tubes. An apparatus has been designed in which protection from atmospheric contamination can be secured by a mercury seal throughout the experiment.

It has been found that the presence of argon in the residual gases furnishes an exceedingly sensitive test for

atmospheric contamination, and that a mercury seal can only be relied on if precautions are taken to ensure that the mercury and glass are scrupulously clean.

The author has not been successful in reproducing the conditions necessary for the production of neon and helium.

"Analysis of Gases after Passage of Electric Discharges."

By A. C. G. EGERTON.

"Dilute Solutions of Aluminium in Gold."

By C. T. HEYCOCK, F.R.S., and F. H. NEVILLE, F.R.S.

"Variation of Electrical Potential across a Semipermeable Membrane." By Prof. F. G. DONNAN, F.R.S., and G. M. GREEN.

"Potential of Ellipsoidal Bodies and the Figures of Equilibrium of Rotating Liquid Masses." By J. H. JEANS, F.R.S.

It will be remembered that Sir G. Darwin was convinced that the pear-shaped series of figures of equilibrium discovered by Poincaré was initially stable, while M. Liapounoff had with equal conviction announced that it was unstable. The present investigation was undertaken primarily in the hope of deciding between these two views.

The main conclusion arrived at is somewhat disappointing. It is that, in spite of the labours of Poincaré, Darwin, and Liapounoff, we have still no definite knowledge as to the stability or instability of the pear-shaped figure.

All these investigators have worked at the question of the stability of the pear-shaped figure carried as far as the second order of small quantities. The present paper indicates that, as far as second-order terms, there are a doubly-infinite series of such figures which can, of course, be broken up into linear series in as many ways as we please. As far as can be seen, Sir G. Darwin has concerned himself with only one of these series, while M. Liapounoff has presumably dealt with a different series. It appears that the true linear series demanded by the general theory of Poincaré (*Act. Math.*, vii., 295) only reveals itself when the computations are carried as far as the third order of small quantities, a conclusion which is confirmed by the result of a previous investigation on the figures of equilibrium of rotating cylinders (*Phil. Trans.*, A, 1902, cc., 67). Thus, an investigation of the stability of the pear shaped figure appears to necessitate a calculation of this figure as far as the third-order terms, and this, in turn, demands a method of writing down the potential of a distorted ellipsoid to the third order. The present paper contains such a method; it is illustrated by the computation of the figure of equilibrium as far as second-order terms, and in this way the existence of the doubly-infinite series of figures is revealed.

"The 27-day Period in Magnetic Phenomena." By Dr. C. CHREE, F.R.S.

The author has dealt in two previous papers in the *Philosophical Transactions* with data which seemed to confirm the reality of a period of about 27 days in magnetic phenomena, in the sense that if any particular day is more than ordinarily disturbed, or more than ordinarily quiet, the day which is 27 days later shows a decided bent in the same direction. In these investigations use was made almost entirely of magnetic "character" figures. As international "character" figures do not exist for years prior to 1906, and as "character" figures assigned at one station are open to certain objections, it appeared desirable to ascertain whether or not the 27-day period is clearly shown in the average year by the amplitude of the daily ranges of the magnetic elements. This is investigated in the present paper, use being made of the Kew declination horizontal force and vertical force ranges from 1890 to 1900, treated independently. The period is found to be clearly shown by the range of each element.

"Electrification of Water by Splashing and Spraying." By J. J. NOLAN.

Water is broken into fine drops—(1) by allowing it to fall into a horizontal air stream of high velocity; (2) by spraying. The size of the drops and the charge per cc. of water are measured. The conditions of the experiments enable measurements to be made for drops of different sizes.

It is found that the charge is positive and inversely proportional to the radius of the drops. This result follows if we assume that there is a constant charge produced per unit area of new water surface formed. The value of this constant is approximately 2.7×10^{-3} electrostatic units for distilled water, the splashing and spraying methods giving identical results.

"Effect of Pressure upon Arc Spectra. No. 5." By W. G. DUFFIELD.

"Measurement of Alternating Electric Currents of High Frequency." By A. CAMPBELL and D. W. DYE.

As the accurate measurement of currents larger than 1 ampère at high frequencies presents considerable difficulty, the authors have investigated the accuracy obtainable in the use of air-core current transformers (suggested by Mr. T. L. Eckersley). It is found that, with proper design, such transformers allow of the measurement of currents up to 50 amperes or higher, at frequencies from 50,000 up to 2,000,000 per second, with an accuracy of 1 or 2 parts in 1000. Over the same range of frequency it is also found that iron-cored transformers can easily be designed so as to give very accurate results. As an auxiliary standard for measuring high frequency currents of about 1 to 5 amperes a thermal ammeter was used, consisting of a heater wire and thermopile both immersed in oil, the pile being connected to a low-resistance galvanometer. With this instrument a scale almost exactly proportional to the current (and not to its square) could be obtained.

"The Trypanosome causing Disease in Man in Nyasaland." By Surg.-Gen. Sir D. BRUCE, Maj. A. E. HAMERTON, Capt. D. P. WATSON, and Lady BRUCE.

- (1) The Liwonde Stain. Part I. Morphology. Part II. Susceptibility of Animals.
- (2) The Naturally Infected Dog Strain. Part I. Morphology.
- (3) Susceptibility of Animals to the Naturally Infected Dog Strain.
- (4) Morphology of Various Strains. The Human Strain. VI.—X.
- (5) II. The Wild Game Strain. III. The Wild *Glossina morsitans* Strain. Part II. Susceptibility of Animals.
- (6) The Naturally Infected Dog Strain. Part III. Development in *Glossina morsitans*.
- (7) The Naturally Infected Dog Strain. Part IV. Experiments on Immunity.

"Origin of the Electron Emission from Glowing Solids." By Dr. F. HORTON.

"Sources of Disturbance of the Normal Atmospheric Potential Gradient." By W. A. D. RUDGE.

"Theory of the Nature of Cancers and of their Treatment by Radio-therapy." By Prof. J. JOLY, F.R.S.

"Morphological Studies of Benzene Derivatives. VI. Parasulphonic Derivatives of Chloro-, Bromo-, Iodo-, and Cyanobenzene." By C. S. MUMMERY.

"Absorption of Gases in the Discharge Tube." By F. H. NEWMAN.

"Further Observations on the Changes in the Breathing and the Blood at Various High Altitudes." By Miss M. P. FITZGERALD.

"Experiments on Inheritance in Parthenogenesis." By W. E. AGAR.

"Influence of Timbre and Loudness on the Localisation of Sounds." By C. S. MYERS.

"(1) Conductivity of Salt Vapours. (2) Ionisation produced by Gas Reactions." By S. J. KALANDYK. The experiments described in (1) show:—

1. The conductivity of the salt vapours is due to the processes occurring in the vapours themselves.

2. The vapours of carefully dried salts conduct the electric current. Therefore the conductivity cannot be ascribed to the chemical action of water vapour in the salt vapours. However, the presence of water vapour increases the current passing in salt vapours.

3. When cadmium iodide was very carefully dried it was possible to observe a current which was practically independent of time.

4. The connection between the current i and the temperature θ may be expressed with considerable accuracy by the formula $i = ae^{-\frac{\theta}{b}}$ where a and b are constants.

5. The ionising potential calculated from the energy of dissociation is considerably less than for the ordinary gases.

6. The dissociation of vapours is not always accompanied by ionisation.

"Excitation of γ -Rays by β -Rays." By H. RICHARDSON.

"Growth of Metallic Eutectics." By F. E. E. LAMPOUGH and J. T. SCOTT.

"Wave-lengths of Hydrogen Lines and Determination of the Series Constant." By W. E. CURTIS.

1. The wave-lengths in I.A. of the first six lines of the hydrogen series have been determined with an accuracy of about 0.001 A.U.

2. Balmer's formula has been found to be inexact. The results may be represented by a modified Rydberg formula containing only two constants, thus:—

$$n = \frac{N}{4} - \frac{N}{(m + \mu)^2}$$

where

$$N = 109,679.22$$

and

$$\mu = +0.0569.$$

3. An accuracy of 0.001 A.U. is attainable in the third order of a 10-foot concave grating if the exposures are short (say less than half-an-hour). With longer exposures accurate determinations become very difficult if the temperature of the instrument cannot be controlled.

4. The tertiary iron arc standards determined by Burns were tested in the special regions under investigation, and found very satisfactory.

"Constancy of the Optimum Temperature of an Enzyme under Varying Concentrations of Substrate and of Enzyme." By A. COMPTON.

"Capacity for Heat of Metals at Low Temperatures." By Dr. E. H. GRIFFITHS, F.R.S., and EZER GRIFFITHS.

An account is given of an investigation into the capacity for heat of some metals at various points in the range 0° to -160° C.

A new method of obtaining constant temperatures is described in which the Joule-Thomson cooling effect on expansion of air is utilised.

The formulæ of Einstein, Nernst, and Lindemann, and Debye are compared with the experimental results over a very extended range of temperature.

None of these formulæ, however, can be regarded as completely representing the experimental results.

"The Excitatory Process in the Dog's Auricle." By T. LEWIS, J. MEAKINS, and P. D. WHITE.

"(1) Observations on the Composition and Derivatives of Urinary Dextrin. (2) The So-called Lævulose met with in Urine." By Dr. P. J. CAMMIDGE and H. A. H. HOWARD.

"The Silver Voltameter. Part III. The Solvent Properties of Silver Nitrate Solutions." By T. M. LOWRY, F.R.S.

"Fog Signals—Areas of Silence and Greatest Range of Sound." By A. MALLOCK, F.R.S.

"Osmotic Data in Relation to Progressive Hydration." By W. R. BOUSFIELD.

"Lunar Diurnal Variation of the Earth's Magnetism at Pavlovsk and Pola (1897—1903)." By Dr. S. CHAPMAN.

"Interpretation of the Indications of Atomic Structure presented by Crystals when interposed in the Path of X-Rays." By W. BARLOW, F.R.S.

"Fluorescence of Iodine Vapour excited by Ultra-Violet Light." By Prof. J. C. McCLENNAN.

"Influence of Molecular Constitution and Temperature on Magnetic Susceptibility. Part III. Molecular Field in Dia-magnetic Substances." By A. E. OXLEY.

"Diffusion of Hydrogen through Palladium." By A. HOLT.

PHYSICAL SOCIETY.

June 20, 1914 (at the Cavendish Laboratory, Cambridge).

Sir J. J. THOMSON, O.M., F.R.S., President, in the Chair.

A PAPER entitled "Production of Very Soft Röntgen Radiation by the Impact of Positive and Slow Cathode Rays" was read by the PRESIDENT.

Röntgen and his pupils had always held that light waves were identical in nature with electrical waves produced by mechanical means, but there was a gap, on which very little work had been done, between the longest infra-red radiation and the shortest electrical wave that could be mechanically produced. He believed the investigation of this gap to be essential to the proper study of the constitution of the atom. The work already done on X-rays had demonstrated the existence of two separate rings of electrons in the atom, one within the other. These rings were responsible for the K and L types of radiation respectively. The L radiation was so much softer than the K that if a third ring of electrons existed, the radiation from which was proportionately softer than that of the L type, this radiation would fall well within the gap already mentioned.

In the first experiment described a special form of discharge tube was employed. The positive rays passed through a tubular perforation in the cathode and impinged obliquely on a metal target. A photographic plate of the Schumann type was situated at the further end of a branch tube in such a position that no solid obstacle interposed between the target and the plate. When the discharge passed between the electrodes, the photographic plate was affected. The application of an intense transverse electrostatic field between two metal plates situated between the cathode and the target completely stopped the effect, showing that this was not due to stray radiation reflected from the target, since, while charged particles would be swept to one side, radiation would not be affected by the field. Hence the passage of positive particles from the cathode to the target was essential. On the other hand, a strong transverse electrostatic field in the branch tube had no effect, showing that a radiation was passing between the target and the plate, which was not, therefore, merely affected by positive particles rebounding down the side tube after impact on the target.

The properties of this radiation were intermediate between ordinary X-rays and Schumann waves. They were susceptible to reflection by metal surfaces, and their penetrating power was very small. They were completely stopped by the finest collodion film obtainable.

It was shown that the quality of the radiation did not

depend on the energy of the moving particles which gave rise to it, but on the velocity. Hence equally soft rays should be produced by cathode particles if these were travelling as slowly as the positive rays. A discharge tube was constructed in which the cathode rays, leaving the cathode with the ordinary velocity, could be subjected to a retarding electrostatic field of variable strength before impinging on the target. In this way the velocity of impact could be varied over a large range, and radiations were obtained varying in quality from ordinary hard X-rays to the so-called Schumann waves. It was hoped by the study of these radiations to be able to determine not only the number of rings of electrons within the atom, but the number of electrons in each ring.

DISCUSSION.

Sir OLIVER LODGE expressed the opinion that the work just described was of far-reaching importance, and he felt confident that the results warranted the anticipation that further work would confirm the explanation foreshadowed by the President. The full meaning of the experiments and the way in which they enabled us to estimate the number of rings in the atom was given to some extent in previous papers by the President and others. Eventually we would understand the argument more fully, and in this way the unravelling of the secret of the atom would be materially advanced.

A paper "*On the Homogeneity of Atmospheric Neon*" was read by Mr. F. W. ASTON.

Dr. A. RUSSELL proposed a vote of thanks to Sir Joseph and Lady Thomson for their kindness in taking so much trouble to ensure the success of the Society's visit to Cambridge.

The vote was carried with enthusiasm.

June 26, 1914 (at the Imperial College of Science).

Dr. A. RUSSELL, Vice-President, in the Chair.

A paper entitled "*On Atmospheric Refraction and its Bearing on the Transmission of Electromagnetic Waves round the Earth's Surface*" was read by Prof. J. A. FLEMING.

In this paper the author considers the conditions under which true atmospheric refraction would be sufficient to carry a ray of light or electromagnetic radiation sent out horizontally from any point on the earth's surface round the earth parallel to its surface. It is now generally agreed that pure diffraction is insufficient to account for all the phenomena of long-distance wireless telegraphy, but that we have to postulate some action of the atmosphere which tends to curve the radiation round the earth. The theory of ionic refraction has been put forward, which is based on the theoretical conclusion that in ionised air the velocity of long electric waves is increased. We know as a matter of fact that the atmosphere decreases in density as we rise upwards, and this alone produces a decrease of refractive index and an increase in velocity.

The first part of the paper is concerned with the deduction of formulæ expressing this variation of density with heights taking into account as far as possible the known temperature variation with increase of height. It is shown that at a height of 100 km. the terrestrial atmosphere must consist substantially of hydrogen and helium. An expression is then obtained for the radius of curvature at any point of a ray of light sent out horizontally from the earth's surface, and it is shown that this radius at the starting-point is given by the formula $\rho = \mu_0 / (98Aq_0^2)$, where μ_0 and q_0 are the refractive index and density at the surface of the earth, and A is the Gladstone and Dale constant for the gas which forms the atmosphere. From known values for various gases it is shown that for air ρ is four times the earth's radius, for hydrogen 136 times, and for krypton equal to the earth's radius. Accordingly if the terrestrial atmosphere consisted wholly of krypton a

ray sent out horizontally would be refracted round the earth, and in such an atmosphere wireless telegraphy to the Antipodes would be possible. The above formulæ are deduced in three ways. It is also shown that for the same atmospheric density and constant A this circular refraction would result if the earth were twice its present diameter.

The question of atmospheric composition is then considered in the light of what is known about the auroral spectrum. The suggestion is made that perhaps the non-valent gases neon and krypton are manufactured at great atmospheric heights by electric discharges occurring in the rarefied hydrogen atmosphere. Also that by their ease of ionisation they contribute to produce the ionised layer demanded by the theories of Heaviside and Eccles to account for the actual achievements of long-distance wireless telegraphy.

Finally, it is suggested that our earth is perhaps unique in being the only planet on which such long-distance radiotelegraphy is possible.

DISCUSSION.

Mr. DUDELL considered it was very difficult to follow what was going on in long-distance transmission. One difficulty was that it seemed probable that the heavier gases were absent from the upper atmosphere, yet we had to assume their presence either to get the refraction effect or the Eccles effect.

Dr. C. CHREE thought Prof. Fleming's paper emphasised the importance of the field common to meteorology and wireless telegraphy. With regard to the relations between temperature, pressure, and altitude in the atmosphere, aqueous vapour was an element which meteorologists had to take serious account of; its variability exercised a great influence on the results within 2 km. or 3 km. of the ground. With respect to the constitution of the upper atmosphere, more or less successful attempts had been made of late years to obtain samples by means of apparatus sent up by pilot balloons. On the theoretical side, there were papers more recent than the pioneer one by Sir James Dewar quoted by Dr. Fleming. In particular he would call attention to two papers by Wegener in the *Physikalische Zeitschrift* for 1911. A fundamental point was whether the auroral spectrum did or did not connote a gas different from all hitherto isolated at the earth's surface. Wegener thought it did, and believed the unknown gas thus indicated to be a very light one, which at great heights was even more important than hydrogen. The fact that Prof. Störmer's recent photographic determination of auroral heights had in some cases supplied heights well over 300 km. was evidence that an atmosphere of some kind extended to a very great height. The fact emphasised by Dr. Fleming that wireless results by day and night differed markedly certainly seemed to support strongly his contention that the upper atmosphere played a most important part in the phenomenon. A similar conclusion had been drawn in the case of the ordinary diurnal variation of the elements of terrestrial magnetism, where normally changes were much larger by day than by night, and much larger in summer than winter. It had been found, however, that while the difference between mid-summer and midwinter existed in high altitudes, the difference between night and day was there much reduced, even at the equinoxes. Systematic wireless observations in the Arctic or Antarctic might throw a great deal of light upon the whole question.

Prof. G. W. O. HOWE congratulated Prof. Fleming on his interesting and suggestive paper, and pointed out that although the upper atmosphere undoubtedly had a profound effect on the transmission of electromagnetic waves over long distances, they were still uncertain to what extent long-distance radiotelegraphy would be possible without any assistance from the upper atmosphere. As successive mathematicians attacked the problem errors were discovered in the previous work, and up to the present the effect of the correction seemed to have been in every

case to increase the amount of energy diffracted around the globe.

Prof. C. H. LEES mentioned that in the formula $(\mu - 1)/q = A$, the value assumed for μ was for sodium light, whereas the value required was for $\lambda = 500$ metres.

Prof. MARCHANT mentioned that in some work recently published it was shown that the difference between the carrying power of signals by night and by day was very much greater in summer than in winter. He asked within what limits of accuracy Gladstone and Dale's law held.

Prof. FLEMING, in reply, said that Dr. Chree's remarks were of importance, and the questions raised required to be cleared up. In reply to Dr. Lees, he said that for all gases the square root of the dielectric constant for steady voltage practically agreed with the refractive index for sodium light. It would be useful to have the known facts as to the nature of the atmosphere collected for the use of wireless investigators.

A paper on "Atmospheric Electricity Observations made at Kew Observatory," by Dr. GORDON DOBSON, was read by Dr. C. CHREE.

The paper gives an account of experiments made to determine the accuracy of the results obtained with the apparatus designed by Mr. C. T. R. Wilson for measuring the electric conductivity of the air, and the electric current passing from the air to the earth. Observations were made (1) using the standard instrument on a stand according to the usual practice and (2) using an experimental apparatus level with the ground, which was assumed to give correct results. It was found that it was necessary to apply a small correction to the results obtained with the standard apparatus when used in the ordinary way.

A comparison was also made of the electric conductivity of the air as measured by Mr. Wilson's apparatus and that designed by Prof. Ebert. The results given by this latter apparatus appear to be too inaccurate to allow any satisfactory conclusions to be drawn.

DISCUSSION.

Prof. C. H. LEES said it was important to settle which was the better of the two methods. He thought the large Langevin ions were at the root of the trouble.

Dr. CHREE said the large ions considerably affected the charge per unit volume, but he did not think they would affect the value of the earth-air current.

A paper on "Thermal and Electrical Conductivities of some of the Rarer Metals and Alloys" was read by Mr. T. BARRATT.

A new method of the "stationary temperature" type is employed for measuring the thermal conductivities of some of the rarer metals, including tantalum, molybdenum, rhodium, iridium, and tungsten, at air temperatures and at 100°C .

It is shown that if a rod of metal is of length l , perimeter p , and cross-section q , then its thermal conductivity k is given by—

$$k = \frac{H^2}{pqhV^2} \coth^2 al,$$

where H is the heat given per second to one end of the rod, V the excess of temperature of this end over that of the enclosure, h the heat lost per second from 1 sq. cm. of surface when its excess of temperature over that of its surroundings is 1°C ., and $a = \sqrt{\frac{hp}{qk}}$.

If l is large the equation reduces to the very simple form $k = \sqrt{\frac{H^2}{pqhV^2}}$ this latter equation being employed in nearly every case.

Experimental details and the method of working out the results are given, and it is shown that the thermal conductivity of non-metals can also be determined in the same way.

Electrical conductivities of the same specimens have also been measured, and, for purposes of comparison

with electronic theories, the values of k/KT have been worked out, where k = thermal conductivity, K = electrical conductivity, and T = absolute temperature.

DISCUSSION.

Prof. C. H. LEES thought the method extremely useful and simple. The accuracy obtained was quite sufficient to allow of verification of the ionic theories on which the author touched. His figures differed sufficiently from the theoretical value to show that the theory was only approximate in its present state.

Dr. HARKER asked about the uniformity of temperature in the air space. The apparatus was horizontal, and if the heat supplied to the wire was very great there were bound to be considerable irregularities of temperature in the chamber.

Mr. BARRATT, in reply to Dr. Harker, said there was sometimes a very slow change of temperature of the air in the enclosure, but as the actual experiments, once conditions had become steady, took only a few minutes, the small change in temperature would not matter. Moreover, this change would affect both the hot end of the specimen and the cold one, so that the value of V , which was the object of the measurement, would not be altered. The same remark applied to the temperatures at the top and bottom of the water-jacket. So long as the platinum thermometer was kept in the same place the measurement of V was unaffected.

A paper entitled "Some Investigations on the Arc as a Generator of High-frequency Oscillations," by Mr. F. MERCER, was read by Prof. MARCHANT.

This paper contains the results of a series of experiments on the copper carbon arc when used as a generator of high-frequency oscillations. The copper electrode was water-cooled, and the whole enclosed in a cast-iron cylinder filled with hydrogen under pressure.

Preliminary experiments were carried out to determine the conditions which would give maximum steadiness of burning, and in the ensuing experiments these conditions were adhered to as rigidly as was possible.

The first experiments deal with the effect of varying the arc length, and also the arc current (by changing the resistance in series with the arc), on the magnitude and frequency of the shunt current. The deduction is drawn that the effect on frequency arises from a change in the resistance of the arc.

The second experiment refers to the effect on the shunt current of altering the ratio of inductance to capacity. Keeping the latter constant and varying the former a series of curves were obtained, showing that for a given capacity there is a certain value of inductance giving maximum current in the shunt circuit.

Experiments were also made to determine the effect which the pressure of the hydrogen would have on the magnitude of the shunt current. This is dependent on the P.D. used. With small P.D.s the effect is negligible, at 1000 volts it is just appreciable, and at 2000 volts a marked increase is apparent. Beyond this it was impossible to obtain readings with any degree of accuracy, as the oscillations were very unsteady.

DISCUSSION.

Prof. FLEMING mentioned that Mr. Bairsto had used an arc under pressure as a source of high-frequency oscillations over a year ago. He then described a more satisfactory method recently used by himself and Mr. Coursey. A number of carbons were fixed vertically to a metal plate which was suspended near the bottom of an iron vessel containing heavy oil. The carbons just project above the oil. Over each carbon tip is suspended a copper cylinder, the walls of which go down into the oil, and the thick top of which is perforated. Arcs are struck by lowering the cylinders until they make contact with the carbons, and then raising them with a screw. In this way very steady oscillations were obtained.

Mr. DUDELL said that the Society was indebted to Dr. Marchant, who had come from Liverpool purposely to

read Mr. Mercer's paper. Many of the observations mentioned in the paper were common knowledge to those who had worked with arcs. He would like, however, to call attention to the peculiar shape of the curves connecting the current in the shunt circuit and the frequency which the author had obtained, and in this connection he would like to ask the author whether the oscillations were of what are known as the first or the second type. If the latter were the case, it might be possible to explain the peaks on the curve, and that their position would probably depend on the relation between the self-induction in the main circuit and the capacity in the shunt circuit.

Mr. E. H. RAYNER asked what was the source of supply, and whether large amounts of inductance and resistance were used between the arc and source of power, as it might be that the character of the curves obtained might be modified if the "ballasting" in this part of the circuit were small. He also asked whether any attempt was made to load up the oscillating circuit with resistance to represent power radiated or otherwise employed. One would expect some modification in the results as compared with a "frictionless" oscillating system.

Prof. MARCHANT, in reply, expressed his interest in Prof. Fleming's generator. The author had found that when the power was too great the arc became unstable. He thought Mr. Duddell's explanation was probably correct, as the oscillations were of the second type. It was noticed that with a big capacity, the peak was considerably less pronounced. There was a constant inductance in the circuit, and the current was reduced by adding resistance.

NOTICES OF BOOKS.

X Rays. By G. W. C. KAYE, B.A., D.Sc. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1914.

THIS book gives a highly interesting account of the investigation of X-rays, and can be recommended for the non-specialist who wishes to keep abreast of modern work, as well as for the student of physics. The treatment of the subject is descriptive and non-mathematical, and the most recent research on the Interference and Reflection of X-rays is admirably described. Some account is given of the practical applications of the rays, and one chapter is devoted to an excellent discussion of their nature.

Twelfth Annual Report of the Bureau of Science, Philippine Islands. By ALVIN J. COX. Manila: Bureau of Printing. 1913.

ALTHOUGH the Bureau of Science of the Philippine Islands is only a young institution, and, moreover, had in its early years many difficulties to contend with, it is doing valuable scientific work, thanks to its excellent organisation and management. Its publications on all branches of science have won it an international reputation, which is all the more remarkable because much of the time of the workers is taken up with routine analyses and examinations. By the pathological work carried out in the biological laboratory valuable information is being acquired, and the need for more room and more workers is becoming urgent. The allocation of additional public funds to the Bureau would be well repaid, and all who read the report of its work will agree that it thoroughly deserves recognition and support.

Chemical Calculations. By H. W. BAUSOR, M.A., *Chemical Calculations (Advanced Course).* By H. W. BAUSOR, M.A. London: University Tutorial Press. Ltd. 1914.

THE use of these books will give the student of chemistry much assistance in overcoming the difficulties in working out calculations often experienced by beginners. In the

first volume a number of worked problems dealing with the gas laws, solubility, chemical equations, and volumetric and gravimetric analysis are given. The methods adopted are always clear, and short explanations of the principles involved are provided. About 200 unworked examples are also given. These have been specially written for the book, and are carefully graduated. The advanced course deals with molecular weight determinations and problems in thermochemistry, the latter subject being treated very fully and thoroughly. Both books contain logarithm and atomic weight tables, and are provided with answers to the problems.

Kinetische Stereochemie der Kohlenstoffverbindungen. ("Kinetic Stereochemistry of the Carbon Compounds"). By Dr. ARTHUR VON WEINBERG. Braunschweig: Friedrich Vieweg und Sohn. 1914. (M. 3).

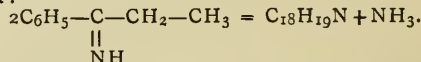
THE aim of this book is to show what light the theory of atomic motion throws upon the problem of the nature of chemical processes, and without going very deeply into the question the author gives a clear summary of modern theories. On the assumption of vibratory and rotatory atomic motion he shows how various phenomena, such as optical activity, desmotropism, &c., may be explained, and the application of the theory to the aromatic series is discussed fairly fully. The kinetic theory of organic dyes can be only briefly alluded to, for to treat the subject in anything like full detail would require a whole book. The conception of the asymmetric carbon atom, which has a rotatory movement about an axis which moves in a cone, is clearly explained, and the book gives an interesting insight into the views of an eminent adherent of the school of Baeyer and van't Hoff.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 20, May 18, 1914.

Ketoisoketiminines, a New Class of Nitrogenous Substances.—Charles Moureu and Georges Mignonac.—Phenylethylketimine is unstable and readily undergoes condensation with elimination of 1 molecule of ammonia:—



The product is a member of a new class of nitrogenous substances for which the author proposes the name ketoisoketiminines. From its reactions it is evident that it contains the group $-\text{C}-$, i.e., the residue of the true cetimine

group $\begin{array}{c} \parallel \\ \text{N} \\ | \\ -\text{C}- \end{array}$, as well as that of the isoketimine group.

The ketoisoketimine group is that of pyridine, which in its annular form may be written $\begin{array}{c} \text{C} \quad \parallel \\ \diagdown \quad \diagup \\ \text{N} \end{array}$, and thus pyridine is a ketoisoketimine which is stable because its functional group forms a constitutive part of a cyclic nucleus.

Constitution of Galegine.—Georges Tanret.—Galegine, the alkaloid obtained from the seeds of *Galega officinalis*, has the formula $\text{C}_6\text{H}_{13}\text{N}_3$. It appears to be formed by the union of a molecule of 3-methylpyrrolidine and a molecule of urea, a molecule of water being eliminated. Or it may be regarded as having been formed by the condensation of methylpyrrolidine with guanidine, a molecule of ammonia having been eliminated. When hydrolysed it splits into 3-methylpyrrolidine and urea.

THE CHEMICAL NEWS.

VOL. CX., No. 2852.

A REGULARITY BETWEEN MOLECULAR HEAT OF COMBUSTION AND ITS BEARING ON THE CONSTITUTION OF THE HYDROCARBONS.

By GERVAISE LE BAS, B.Sc.

(Concluded from p. 27).

THE M.H.C. of the above compounds show that unsaturation in a material sense may be accompanied by unsaturation as regards energy, by which we mean energy which is not fixed by action on other matter necessary for the material saturation of the compound.

We may, however, have a compound quite saturated as regards its composition, and yet be unsaturated in the sense which we have indicated. The evidence for this is derived from a study of the polymethylenes.

Gaseous trimethylene, C_3H_6 .

$CH_2 \begin{array}{c} \diagup CH_2 \\ \\ \diagdown CH_2 \end{array}$	M.H.C.	499.6	$\Delta = +23.0$ for unsat.
Σn A.C.		476.6	

We may indicate the values of all the various liquid polymethylenes by noting that the heats of combustion of the polymethylene dicarboxylic acids are similar to those of the hydrocarbons themselves.

It is a general rule that the heats of combustion of the carboxylic acids are similar to the heats of combustion of the hydrocarbons which would be formed by subtracting CO_2 therefrom. The polymethylene carboxylic series thus resembles that of the polymethylene, and the carboxylic acid derivatives of the reduction products of benzene show similar characteristics to those of the parent hydrocarbons.

Trimethylene, 483.3 (liquid)	Trimethylene dicarboxylic acid, 483.0
Tetramethylene, —	Tetramethylene dicarboxylic acid, 642.0
Pentamethylene, 780.0	Pentamethylene dicarboxylic acid, 776.0
Hexamethylene, 933.8	Hexamethylene dicarboxylic acid, —

The value of (H) is about 26.0.

Liquid Polymethylenes.

$C_n C_{2n}$	M.H.C.	n.	$n \times 26.0$	Δ .
C_3H_6 ..	483.3	18	468.0	+15.3
C_4H_8 ..	642.0	24	624.0	+18.0
C_5H_{10} ..	780.0	30	780.0	—
C_6H_{12} ..	933.8	36	936.0	—

The above calculated differences represent a definite amount of weakness in the single linkings of tri- and tetramethylene, and this is illustrated by the well-known instability of these hydrocarbons. Pentamethylene and hexamethylene are shown to be saturated, and in accordance with this are stable structures.

On this circumstance Baeyer founded his well-known strain theory (*Ber.*, 1885, xviii., 2278; 1890, xxiii., 1275). The deviations of the direction of attraction from the normal, as indicated by the directions of the valency linkings in the tetrahedral arrangement, can easily be calculated. These deviations according to Baeyer are a measure of the strain, and consequently of the instability.

Measures of Deviations of Directions of Attraction and Instability in Various Compounds.

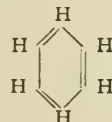
	Deviation.	+ Δ in heat of comb.
—CH : CH— ..	54° 44'	+15.6 (gas)
Trimethylene ..	24 44	+23.0 (gas) +15.3 (liquid)
Tetramethylene ..	9 44	— +18.0 (liquid)
Pentamethylene ..	0 44	—
Hexamethylene ..	-5 16	—

If we are to accept Bayer's hypothesis as a complete explanation of the phenomena, it will be necessary to account for the following facts. According to the strain theory trimethylene ought to be more stable than ethylene, for instance. Nevertheless it is found to be less stable. This is quite in accord with the greater magnitude of the difference for the former as compared with the latter. Thus when burnt as gases—

Propylene, $CH_3.CH:CH_2$..	M.H.C.	492.0
Trimethylene, $\begin{array}{c} CH_2 \\ \\ CH_2 \end{array} CH_2$..		499.0
	Δ	+7.0

The value for the latter is 7 k. greater than that for the olefin.

Again, if the benzene molecule possesses the formula given to it by Kekulé—



then, according to Baeyer, we must expect instability with corresponding augmentation of the M.H.C.; for though the single link may not account for any appreciable amount of strain, yet two valency linkings similarly directed as in the double bond of Kekulé's formula must occasion a considerable amount, and so render the molecule correspondingly unstable. In fact, the arrangement does not differ in any respect from an ordinary olefin linking. We should thus expect an augmentation in the M.H.C. for each double link, equivalent, as will be shown, to 8 K, or 24 K altogether. That this is not so is indicated by the following table, which illustrates the 4 : 1 Rule :—

The M.H.C. of Benzene and its Derivatives.

Hydrocarbon.	M.H.C.	n.	$\frac{M.H.C.}{n}$
Benzene, C_6H_6 ..	779.8	30	26.0
Toluene, $C_6H_5.CH_3$..	933.8	36	25.9
Hexamethylene, C_6H_{12} ..	933.2	36	25.9
Ethyl benzene, $C_6H_5.C_2H_5$..	1091.0	42	25.9
Hexahydrotoluene, $C_6H_{11}.CH_3$	1095.0	42	26.0

These results reveal the fact that benzene and its homologues are saturated substances, and the arrangement of the atoms must be such as to favour a considerable amount of stability. Incidentally it may be remarked that the M.H.C. of C_6H_{12} is similar to that of $C_6H_5.CH_3$, a fact which is independent testimony amounting to proof that $6(H) = (CH_2)$. It follows that $(C) = 4(H)$, which the additive relations of the M.H.C. of the paraffins show.

The above data are due to Stohmann, who is also responsible for the following table, which, so far as we know, has never been explained.

M.H.C. of the Benzene Reduction Products.

Hydrocarbon.	M.H.C.	Δ .	B.P.	Δ .
C_6H_6 ..	779.8	68.2	80.4	—
C_6H_8 ..	848.0	44.0	84—86	+5.0
C_6H_{10} ..	892.0	41.2	89—84	-2
C_6H_{12} ..	933.2	58.0	79—79.5	-4
C_6H_{14} ..	991.2		69	-10

Similar differences are to be observed in the carboxylic acid derivatives of the above compounds, and in one or two other series, as specially pointed out by Stohmann. It follows that the reasons for the above differences apply to all the series. The changes as shown by the differences themselves are evidently not similar in character.

They can quite easily be explained by assuming the saturation of benzene and hexamethylene, and the presence of one and two olefin linkings in tetrahydro- and dihydrobenzene respectively. The double bond among such compounds can be shown to be responsible for an augmentation of 8 K.

	M.H.C.	Δ .
Dibenzyl (solid), $C_{14}H_{14}$, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5 \dots$	1811	
Stilbene, $C_{14}H_{12}$ $ = $ $C_6H_5 \cdot CH = CH \cdot C_6H_5 \dots$	1765	46.0
Phenyl propionic acid, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot COOH \dots$	1085.2	
Cinnamic acid, $C_6H_5 \cdot CH : CH \cdot COOH \dots$	1042.0	43.2
	Mean Δ	44.6

This difference is almost identical with that between dihydro- and tetrahydrobenzene, and if $2(H) = 2 \times 26.0 = 52.0$,
 $| = | = 2(H) - \Delta = 52.0 - 44.6 = +7.4$.

Applying this result to the reduction products of benzene we find—

n.		M.H.C.	$n \times 26.0$.	$ = $.	Calculated M.H.C.
30. Benzene, C_6H_6		779.8	780.0	—	780.0
32. Dihydrobenzene, C_6H_8 $ = $		848.0	832.0	2×8.0	848.0
34. Tetrahydrobenzene, C_6H_{10} $ = $		892.0	884.0	1×8.0	892.0
36. Hexahydrobenzene, C_6H_{12}		933.2	936.0	—	936.0
38. Hexane, C_6H_{14} $CH_3 \cdot (CH_2)_2 \cdot CH_3$		991.0	988.0	—	988.0

It is thus perfectly clear that whilst one or two olefin linkings are present in tetrahydro- and dihydrobenzene respectively, benzene does not contain any olefin linkages and behaves as a saturated substance. Moreover, the first two compounds are unstable, but benzene is perfectly stable.

Naphthalene, anthracene, and chrysene are saturated in the same sense, and are also stable.

Olefin and acetylene compounds are unsaturated, and possess free or residual affinity.

The polymethylenes are saturated, and yet some possess residual affinity.

Benzene is unsaturated as regards composition, and does not possess loosely held affinity.

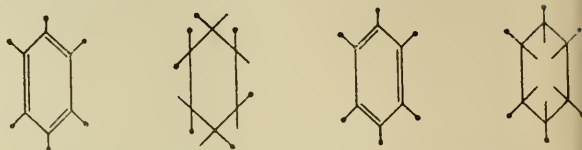
A perfectly satisfactory reason must account for all three. Both the nature of the olefin linking and the structure of benzene have occasioned no small amount of controversy. It is probably not possible to completely solve the incidental difficulties satisfactorily by appealing to any one physical property. It is necessary to deal with the whole evidence, chemical and physical.

The suggested formulæ may be divided into two types—

(a) The mobile valency type, and

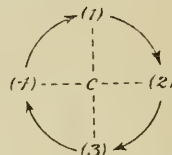
(b) The single-linked fixed valency types.

The first may be grouped together, as Collie, Baly, and others have suggested, and the whole question regarded from a dynamical standpoint. They thus regard the various formulæ as different phases of a cycle of changes—



It should be remembered that the possible vibration of the benzene molecule is not a phenomenon limited to this molecule, but is doubtless a common feature of chemical molecules.

It will be seen that the above changes involve the rotation of the valencies around the C-atoms in the manner indicated by the following diagram:—



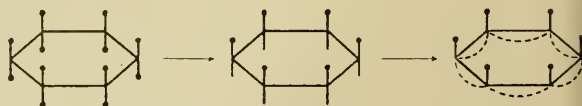
This certainly brings in an atomic property which is not generally recognised, and the flexibility or fluidity implied by the above explanation is contrary to all our notions of atomic structure. The deviation of the valency directions is certainly possible, but probably not spontaneously, for force is necessary to do so.

This mobile valency theory, as applied to benzene, suggests that a considerable amount of free or loosely held energy is a feature of the benzene molecule. This would make the molecule unstable, and affect the different physical properties. Both are contrary to fact.

The different singly-linked saturated types of benzene are the *Diagonal* formula of Claus, the *Prism* formulæ of Ladenburg, the *Octahedral* formula of Thomsen, &c., all emphasise the stability and saturation of the molecule, but it is difficult to realise how reduction could be effected.

The recent formula of Barlow and Pope is deduced from solid crystalline data, and has not been shown to be true under ordinary conditions. It belongs to the type just referred to.

The combination of the two features in the benzene molecule already mentioned is capable of a very plausible explanation. Remembering that the valency links of aromatic and hydroaromatic compounds are not in the plane of the ring, but according to the tetrahedral properties of carbon directed at right angles to it, or at least roughly so, the passage from hexahydrobenzene to benzene by elimination of hydrogen can be represented diagrammatically as follows:—



The free energy which exists when C_6H_{12} is changed to C_6H_6 is evidently fixed in some way, since there are no olefin linkings. Since all the carbon atoms in the benzene molecule are unsaturated, it is reasonable to suppose that it is uniformly distributed between them, an effect which is not possible in the olefins, nor in the reduction products of benzene. This fact is suggested by the third diagram. In this respect it resembles on the one hand an old formula for benzene, based on the heats of combustion, and, on the other, Thiele's formula—



PURITY OF FUSED LITHIUM PERCHLORATE,
AND ITS BEARING UPON
THE ATOMIC WEIGHT OF SILVER.*

By THEODORE W. RICHARDS and MARSHALL W. COX.

In a comprehensive research upon the atomic weights of lithium and silver, H. H. Willard and one of the present authors (Richards and Willard, *Publ. Carnegie Inst.*, No. 125) devised and perfected an entirely new method for determining the latter of the two atomic weights. This method involved the treatment of pure anhydrous lithium chloride with excess of perchloric acid, and the drying of the lithium perchlorate thus formed for a long time in a state of fusion at a temperature of about 300°. From the weights of factor and product, together with the ratio of lithium chloride to silver (determined at the same time in another series of analyses made in the usual way), it is easy to calculate the atomic weight of silver with reference to that of oxygen in the following fashion. Assuming that four times the atomic weight of oxygen is 64.000:—

$$\frac{\text{Ag}}{64.000} = \left(\frac{\text{LiCl}}{\text{LiClO}_4 - \text{LiCl}} \right) \frac{\text{Ag}}{\text{LiCl}}$$

The value of the outcome depends as usual upon the purity of the three solid substances concerned. Silver is capable of being made nowadays in a state of great purity. Lithium chloride also can be prepared in a state very free from contamination, even with water, by methods elaborated at Harvard; but lithium perchlorate, which has been less studied, cannot be heated to a red heat without decomposition, and its freedom from volatile impurities is less certain. This fact was fully appreciated by the experimenters, and they promised to investigate further the question concerning the purity of the lithium perchlorate.

Obviously, any water retained by this salt would decrease the apparent atomic weight of silver, by increasing the denominator of the fraction within the parenthesis. On the other hand, any trace of decomposition suffered by the salt would have the opposite effect. The resulting contamination of the perchlorate by chloride or chlorate is easy to detect; but the retention of minute traces of water is much more difficult to discover. The present investigation, which has been greatly prolonged because of the subtle nature of the problem, has primarily to do with the question as to the anhydrous condition of the lithium perchlorate, and we take pleasure in stating that the question, if not wholly settled, has now at least been carried much further than before. The evidence now available points towards the improbability of the retention of weighable amounts of water by lithium perchlorate at 300°. It is true that this result was not wholly unexpected, for the salt came to satisfactory constancy in weight, even at 280°, and a rise of 30° had no effect upon this weight. Moreover, one of us, in collaboration with G. S. Forbes, showed, some time since, that silver nitrate, a salt nearly as soluble as lithium perchlorate, retained practically no water at all at a much lower temperature, namely, 200°. Nevertheless, the outcome is satisfactory, and leads one to believe that the method under discussion for determining the atomic weight of silver is one of the very best.

At first sight the problem involved in determining the trace of water possibly held by the salt might appear to be a simple one. It is merely necessary to decompose pure lithium perchlorate (which has been fused and dried to constant weight at 300°) and to determine the weight of water which may be evolved among the products of decomposition. But in decomposing a salt by heat under these conditions a portion of the solid is carried along with the stream of gas in a state of subdivision so fine as to evade capture in any ordinary train of purifying towers.

If the complication of this train is greatly increased, the chance of losing a trace of water altogether on the one hand, or fortuitously collecting water from some other source is a serious one.

Two methods of attack were considered. At first it was thought that oxygen and water, and any trace of chlorine evolved, might be condensed together by means of liquid air. The powder would then be held in the condensed liquid, and would doubtless be left behind when the oxygen was allowed to evaporate. (This method was proposed by one of us in 1907, and was used with success in a somewhat analogous case by Stähler and F. Meyer, *Zeit. Anorg. Chem.*, lxxi., 378). The problem of driving the water off from the remaining small amount of solid and collecting it in phosphorus pentoxide would obviously be easy.

After several trials, however, this method was abandoned in favour of another, yet simpler. The gas evolved by decomposing the perchlorate, carrying with it exceedingly fine powder and traces of chlorine, was passed first through a warm coil of closely packed finely divided silver wire to remove the chlorine, and then through a porous porcelain dry-filter or "dust-trap" to remove the powder. The water in the gas thus purified could be easily determined in the usual way.

The coil of silver wire is an old device for the purpose of removing undesired chlorine. Its efficiency was shown by the fact that the portion of the silver nearest to the decomposing salt was tarnished, whereas the greater part of the coil kept its original lustre through many experiments.

The "dust-trap" also is not an entirely new idea. It was used by one of us in collaboration with Köthner and Tiede, in an investigation upon the atomic weight of nitrogen in 1907 (*Zeit. Anorg. Chem.*, 1909, lxi., 320; *Journ. Am. Chem. Soc.*, 1909, xxxi., 6; others also have doubtless employed it). For the present purpose it was necessary to construct a filter which would certainly neither retain a trace of the water nor evolve any into the stream of air passing through it. Moreover, the pores of the filter must be so fine as to allow no appreciable weight of the fine dust from the decomposing salt to pass through them. After a number of experiments we found that a fine-grained unglazed "Pukal" porcelain cup, of the sort used in the coulometer or volameter in 1899 (Richards and Heimrod, *Proc. Am. Acad.*, 1899, xxv., 123; *Zeit. Phys. Chem.*, 1900, xxxii., 339), and since so strongly recommended for the purpose by E. B. Rosa, answers admirably. As a cement to connect this porcelain to the rest of the apparatus, fused silver chloride was found to be the most convenient substance. Each question involved was of course carefully tested. In the first place, a cup (previously cleaned by washing thoroughly with nitric acid and soaking for several days in many portions of distilled water until all acid was removed) was dried in an electric oven, cooled in a desiccator, and weighed. The cup was now moistened with water, and again dried at 300°, cooled, and weighed. This was done three times, with the result that during the whole period the cup remained constant in weight within two-hundredths of a milligram, the limit of the sensibility of the excellent balance used.

In order to test the fineness and evenness of grain of the cup, and to be sure that it was properly cemented to its glass support, it was wholly submerged in water after it had been cemented into place, and air was forced through it under pressure. If small bubbles formed rather slowly over the whole surface of the porcelain, sufficient evidence was obtained that air really passed through the many small passages in the walls, but if a rush of bubbles appeared from one or two points, the cup was obviously imperfect, and was discarded. A similar test might be applied with advantage to cups used for the coulometer. No great trouble was experienced in finding cups which would pass this test; the main difficulty usually appeared where the porcelain was cemented to the glass. Very pure silver chloride, free from any infusible impurities or dust, was

* A brief notice upon this topic was presented to the Eighth International Congress of Applied Chemistry in New York in September, 1912, and printed in the *Original Communications of this Congress*, xxv., 157. From the *Journal of the American Chemical Society*, xxxvi., No. 5.

required to serve as a cement if a perfect joint was to be made.

Obviously it was necessary to collect in a perfectly unaltered condition all the gas emerging from the "dust-trap." Accordingly the porcelain cup was surrounded with a slightly larger glass tube. This wide tube was sealed by an inside joint to the narrow tube bearing the cup, and the open end of the surrounding jacket was drawn down to a small tube which could be connected with the quantitative drying apparatus. The completed dust-trap is shown in Fig. 1; it would allow air to pass under moderate pressure at the rate of two or three ordinary bubbles per second, and maintained its efficiency through a long series of experiments.

The air-filter thus constituted was found to be so efficient in its operation and so free from any disturbing effect that another one of the same type was used in purifying the air used for drying the perchlorate before its decomposition. The fact has long been known that minute particles of dust not visible to the naked eye may be carried in a current of gas through many feet of tubing, or even, in bubbles, through deep layers of liquid. Clearly, then, it is important whenever a substance is to be dried in a considerable current of air, that this dust should be eliminated; for it might easily contaminate to some extent the pure substance to be treated. As will be shown, the outcome in the present case justified these considerations in a striking way, and indicated that in any such case a "dust-trap" of this sort should be employed if the highest accuracy is sought. This outcome in its bearing upon accurate work in general is one of the most interesting of the points enforced by the present research.

The point is most clearly demonstrated by a comparison of the experience of different experimenters upon lithium perchlorate. Potilitzin (see Abegg, "Handbuch der anorganische Chemie," quoting from *Fourm. Russ. Chym. Soc.*, 1888, xx., 1, 541) found that the decomposition of lithium perchlorate into chlorate and chloride proceeded very rapidly at 268°. Richards and Willard were able, on the other hand, to subject the salt to continued treatment at 300° with a barely perceptible trace of decomposition. Their salt and the air with which it was in contact were both doubtless much purer than Potilitzin's; evidently impurities incite catalytic decomposition. At 350° the two Americans found that the salt decomposed so violently as to throw visible particles of dust through several feet of tubing; but in the present research lithium perchlorate dried and fused in a current of carefully filtered air (otherwise precisely similar to that used in the research of 1910), could be heated for three or four hours at 400° with very slight decomposition and with no visible projection of material nor exit of gas. Only at 430° or a higher temperature did decomposition proceed with rapidity or completeness. Moreover, it was possible so to regulate the temperature between 410° and 430° that the decomposition was slow and the current of outgoing gas flowed quite steadily at the rate of from two to three bubbles per second. This previously unobserved stability of lithium perchlorate was doubtless due to the very high degree of purity of the material, probably never before attained; and the chief cause of this purity seems to have been the exclusion of impalpable and invisible dust from the current of many litres of air which passed over the salt during its synthesis, crystallisation, and long-continued drying in a fused condition. The exact mechanism of this catalytic effect cannot be studied quantitatively until the nature of this trace of dust is discovered; possibly the finely powdered steel, which is said to exist in the air of all cities, is responsible. Enough has been said to show that the air-filter served an important office, and to suggest that in other investigations also, where great purity is sought, its help should be employed.

The lithium perchlorate employed in the present work was prepared from very pure materials made several years ago by H. H. Willard and remaining from the research on atomic weights already mentioned. We are greatly

indebted to him for this service. Lithium chloride free from any other base or acid was treated by slight excess of the purest aqueous re-distilled perchloric acid in a flask of fused quartz as described in the earlier research (Richards and Willard, *Publ. Carnegie Inst.*, 1910, No. 125, pp. 39, 40). The evaporation of the water and excess of acid into a current of dry or moist air at gradually rising temperature was also conducted as before. In this way samples of salt fused and dried at 300° were prepared in a condition duplicating closely the portion weighed by the previous investigators. The only difference already mentioned lay in the greater care taken to free the air-current from dust and other impurities. To this end the air, drawn directly from out-of-doors by a water pump, was forced by the same pump over nearly 50 centimetres of hot copper oxide, through two towers containing potassium hydroxide solution containing a little manganate, through other towers containing a little potassium manganate, over fused potassium hydroxide, through another shorter tube of red-hot copper oxide, again over a large quantity of fused potassium hydroxide, over 50 centimetres of the best obtainable phosphoric pentoxide, that had previously been re-sublimed in an electrically heated apparatus, and finally through a dust-trap which was placed just before the flask in which the lithium perchlorate was synthesised. The object of the tube of hot copper oxide was to eliminate the trace of hydrogen or hydrocarbon which may exist in the air of cities; the objects of the other tubes are sufficiently evident without explanation. The air-filter or dust trap was placed at the end of the train so that any dust which might have been carried away from any part of the train itself might be eliminated.

No rubber connections were used in this system; it was all fused together except when the juxtaposition of hard and soft glass necessitated ground joints.

Before attempting to measure any moisture that might be retained by the lithium perchlorate, it was necessary to

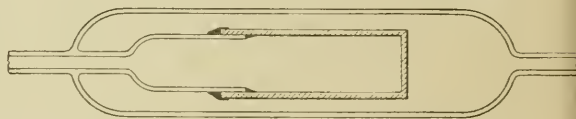


FIG. 1.—DUST-TRAP. (The shaded portion indicates the porous cylinder; the black spots show where silver chloride was used as cement).

prove that no weighable quantity of water passed through this elaborate drying train. The test was effected by means of a weighed U-tube of phosphoric pentoxide as usual. Of course great care was bestowed on the preparation and handling of this tube, since faulty technique here would vitiate the whole work. The tube possessed two tightly fitting glass stopcocks; it had been scrupulously cleaned, and was filled with very pure re-sublimed phosphoric pentoxide. After the work had once begun, this tube was never touched with the hands, but was handled by means of chemically clean cloths or by platinum-tipped forceps. The least possible lubricant of paraffin and fused rubber was used on the stopcocks, and a vanishingly thin layer of the same lined the rubber connectors by which the tube was connected with the train. After a test, only the side-arms of the tube were wiped with several thicknesses of a dry chemically clean cloth. Before each weighing, the U-tube was allowed to remain over night under a bell-jar containing a small dish of sulphuric acid. An exactly similar tube, to be used as a counterpoise, containing glass pearls, was kept under a separate similar bell-jar. Before weighing, the tubes were allowed to adjust themselves to the conditions obtaining in the balance case, the air pressure in both the tube and its counterpoise was made equal to that in the room by very brief opening. An excellent balance, previously used in many atomic weight determinations, was employed, and a tube containing radium bromide was kept in the case, to eliminate electric

charges. Weighing took place by the method of substitution, the two tubes being placed on the balance alternately until perfect equilibrium was obtained. Under such conditions, successive weighings of the tube never but once differed from each other by more than 0.00002 grm., and the single exception was 0.00003 grm. This means that it was possible to weigh the minute quantity of water contained in two or three cubic centimetres of ordinary atmospheric air.

After the long drying train had been swept out with pure air for a number of days, the tube of pentoxide was attached directly to the end of the drying train, in the position usually occupied by the quartz flask of lithium perchlorate, and air was passed through the whole for sixteen hours. During this time the tube gained but 0.00017 grm. in weight. Without allowing the current of air to cease flowing, the empty quartz evaporating flask was placed in position and swept out for eight hours, and the pentoxide tube was attached to the side arm of this flask, while air continued to pass through for sixteen hours more. During this test the tube showed a gain in weight of but 0.00020 grm.—essentially the same amount as before. This quantity appeared to be a constant: two attempts to eliminate even this last trace of water by a condensing coil, submerged in liquid air, were unsuccessful.

The final control experiments were now obtained by placing the tube of silver wire and the second dust-trap in position beyond the quartz flask and passing air through the empty apparatus while the weighed tube of pentoxide was adjusted in its place beyond the dust-trap. Many experiments were made in this way, but in no case could a perfect control experiment be obtained. It is probable that moisture gains access during the fitting up of the apparatus, and the amount seemed to be not very different in protracted experiments from what it was during very brief ones. The gain in weight of the pentoxide tube varied from 0.0002 to somewhat over 0.0003 grm. Two final control experiments made, one just at the beginning, of the series in which lithium perchlorate was decomposed, and one in the middle of that series, were conducted precisely under the conditions maintained in that series, except that in the control experiments no lithium perchlorate was present. In the first of the blank tests the tube of pentoxide gained 0.00028 grm. during five hours; in the second, 0.00034 grm., the average being 0.00031 grm. Although it would have been more satisfactory to find the source of the water, this was not essential for our purpose, since constancy was all that was needed. As time pressed, and it was necessary to hasten the experiments, the decomposition of lithium perchlorate in this complicated apparatus was now undertaken. Five experiments were made; in three of these only a small amount of the salt was decomposed, although it was kept above 385° for over two hours; whereas in the other two experiments more than half of the lithium perchlorate was decomposed. In the first group the procedure was as follows:—Very pure lithium perchlorate, prepared in the quartz flask by the evaporation of lithium chloride with a slight excess of perchloric acid, was heated in a current of dry air for at least five hours at a temperature of 280–300°. This gave samples of the salt in the same condition as the final weighed product of the previous investigators. At this stage the new pieces of apparatus, *i.e.* the tube of silver wire and the dust-trap, were placed in position; and these were swept out over night by the same air that was passing over the lithium perchlorate, which was kept at 200° throughout that time. In the morning, while the current of air continued without interruption, the tube of silver wire was warmed until the hard glass barely showed a sodium flame, and the dust-trap was heated at 150°. At noon, the tube of phosphoric pentoxide, just previously weighed, was securely wired into position, and a protecting tube of pentoxide was added, so as to prevent any moisture from diffusing backwards into the weighed tube. The temperature of the perchlorate was then raised, during an hour, to the maximum used, and was held within 5° of that point

during two hours. Finally the material was gradually cooled to 300°, at which point the pentoxide tube was removed to be weighed the next day. After further cooling, the lithium perchlorate was removed for weighing, so that the extent of its decomposition might be calculated. During the whole experiment, the air pressure in the apparatus was in the outward direction as shown by a mercury manometer sealed into the apparatus at a point just before the air entered the flask of perchlorate. Hence there was very slight opportunity for moist air to penetrate inwards. A new sample of lithium perchlorate was prepared for each experiment, amounting to from 10–15 grms. The maximum temperature was 385° in the first experiment, 400° in the second, 400° in the third. The percentage of decomposition, assuming that all of the decomposed material was converted into chloride, varied from 0.033 per cent in the first to 1.25 per cent in the third experiment. The weight of water caught was in each case slightly less than that found in the control experiments, namely, 0.00020, 0.00027, and 0.00029 grms. Hence no perceptible amount of water was evolved by raising the temperature of the fused perchlorate from 300° to 400°.

In the last two experiments the same procedure as before was followed, except that the perchlorate was heated to a higher temperature, which caused much more far-reaching decomposition. In the fourth experiment, the temperature of 450° was reached after one and one-half hours. At this point the evolution of oxygen was too violent and the experiment had to be stopped. Nevertheless, one would be inclined to think that if any water had existed in the salt it would have been expelled during these ninety minutes; but the tube of pentoxide showed a gain of only 0.00026 grms., or less than that during the control experiments (0.00031).

A fifth experiment was more carefully regulated at between 410° and 430° during two hours, so that all the escaping gas passed through the weighed tube of pentoxide at a rate never exceeding three bubbles per second. The perchlorate (of which about three-quarters were decomposed) evolved bubbles and fine dust continuously, carpeting the whole apparatus as far as the dust-trap with a thick film; but none could be seen beyond the porcelain cup in the trap. The pentoxide tube gained in weight by 0.00039 grms., a trifle more than that shown by the two control experiments (0.00031). It is possible that a trace of the powder, of almost molecular fineness, may have escaped the trap and caused this slight and unimportant difference.

In conclusion, the results show quite clearly that, within the limit of experimental error, no significant quantity of water can be expelled from lithium perchlorate which has been fused to constant weight, even when the temperature is raised to 430°, and most of the salt is decomposed. The first three experiments show an average gain in weight by the tube of pentoxide less than in the control experiments by 0.00006 grm., while the two remaining experiments show an average gain greater than that of the average control experiments by but 0.00002 grm. None of these differences is greater than the probable error of experiment, and even the largest is not large enough to have an important effect in the atomic weight of silver as found by the method of Richards and Willard. A tenth of a milligram of water in 15 grms. of lithium perchlorate would lower the apparent atomic weight of silver calculated with the help of this salt by only about 0.001. Our results therefore seem to afford important evidence in confirmation of the value $Ag = 107.871$, found by those investigators.

A possible source of uncertainty in the interpretation remains to be considered. It is conceivable that a very small amount of water might be retained by lithium perchlorate without dislodgement up to the point of incipient decomposition, and beyond that point held in new combination as lithium hydroxide. Further consideration suggests arguments against this objection, however. We have found that the raising of the temperature by 130° (that is, from 280° to 410°), a change amounting to about one-

fifth of the original absolute temperature, causes no water to be evolved. One would expect that were water present in large enough quantity to be of importance, at least a fraction of it large enough to be detected would have been volatilised before the salt suffered any decomposition at the higher temperature. Again, if any lithium hydroxide had been formed, might it not have attacked the flask, and thus have had its water set free, according to the equation $2\text{LiOH} + \text{SiO}_2 = \text{Li}_2\text{SiO}_3 + \text{H}_2\text{O}$? Usually the susceptibility of the containing vessels to attack is to be regretted, but here it would seem to be possibly more helpful than not.

Although the present paper cannot be considered as more than a preliminary attack upon the problem concerned, it serves to outline the difficulties, and especially emphasises them. With the added knowledge of lithium perchlorate now available, especially in regard to the greater stability of the salt when prepared in a dust-free condition, it will doubtless be possible to obtain an even more accurate evaluation of the ratio of oxygen to lithium chloride and hence of the atomic weight of silver than that found in 1910. It is hoped that this work may soon be undertaken in the Wolcott Gibbs Memorial Laboratory. We take pleasure in expressing our indebtedness to the Carnegie Institution of Washington for generous financial support.

Summary.

1. An effective air-filter or dust-trap for removing impalpable powder from a moderate current of air is described. The importance of its frequent use is emphasised.
2. Lithium perchlorate, prepared entirely in contact with air filtered through this contrivance, was found to be much less easily decomposed by heat than less carefully treated material.
3. The purest lithium perchlorate was found to decompose slowly at from 410° to 430° , and rapidly at 450° .
4. It has been shown that no significant quantity of water can be driven out of fused lithium perchlorate by raising the temperature from 300° to 450° , even although most of the salt is decomposed at the higher temperature.
5. This outcome tends to confirm the use of lithium perchlorate as a basis for determining the ratio of oxygen to silver, and supports the value $\text{Ag} = 107.871$ found by Richards and Willard in 1910.

THE DETERMINATION OF PHENOL IN THE PRESENCE OF HEXAMETHYLENETETRAMINE AND FORMALDEHYDE.

By L. V. REDMAN, A. J. WEITH, and F. P. BROCK.

DURING a research into the rate of condensation between phenols and active methylene groups in the production of synthetic resins it became necessary for us to find a rapid and accurate method for the determination of phenols in

the presence of substances containing methylene groups, e.g., formaldehyde, hexamethylenetetramine, &c.

In previous papers we have described a bromination method which serves for the very accurate and rapid quantitative determination of phenol in a water solution (Redman and Rhodes, *Journ. Ind. Eng. Chem.*, 1912, iv., 655; Redman, Weith, and Brock, *Ibid.*, 1913, v., 389). The method consisted in diluting the phenol to N/1000, in acid solution, shaking the solution for one minute after the bromide-bromate solution is added, then adding KI, shaking again for one minute, and titrating the excess iodine with thiosulphate. The whole operation was carried out at $20-25^\circ\text{C}$.

The present paper deals with the determination of phenol in a water solution in the presence of hexamethylenetetramine or formaldehyde, or both, using the above method with whatever modifications are mentioned later in this paper.

The first of these probable interfering substances to be tried was hexamethylenetetramine, and the results are given in the accompanying table. Hexamethylenetetramine does not interfere in the determination of phenol by bromine when present up to 1 per cent of the total solution; i.e., 30 mols. of hexamethylenetetramine to 1 mol. of phenol. (The total solution refers to the volume after the dilution has been made with the water and acid, before adding the bromine solution). Much larger amounts than this have been tried. As much hexamethylenetetramine as 15 per cent of the total solution, i.e., 450 mols. of hexamethylenetetramine to 1 mol. of phenol, has been added in a single determination of the phenol without changing the results. The only intermediate change noted when the hexamethylenetetramine was present in large quantities was a tendency on the part of the free iodine to form a brick-red granular precipitate, or a beautiful iridescent crystalline precipitate with the excess hexamethylenetetramine. This precipitate, which is either the tetra-iodo-hexamethyltetramine or di-iodo-hexamethyltetramine, dissolves up readily on the addition of the thiosulphate, giving back the free iodine, and does not in any way interfere in the quantitative determination.

The presence of free formaldehyde, however, interferes very seriously with the phenol determination. Results that are 7 to 8 per cent too high are obtained when the total solution is 1 per cent formaldehyde, as is shown in the table (Expts. 5 and 6). The higher the percentage of formaldehyde present the higher the results which are obtained for the phenol present in the solution until, for 40 per cent formaldehyde, bromine is absorbed in very large quantities and no precipitation of tribromophenol takes place, and the determination of phenol by this method is quite impossible.

It is evident then that if hexamethylenetetramine does not interfere with the determination, and formaldehyde does interfere, the addition of ammonia to the solution in which formaldehyde is present as an interfering substance may, by forming hexamethylenetetramine with the aldehyde, obviate the trouble.

No.	Amount of interfering substance.	NH ₃ added. Cc.	Time after ammonia was added, to determination.	HCl added. Cc.	Br solution used. Cc.	Thiosulphate solution used.	Phenol determined. Per cent.
1.	—	0	—	6	16.92	3.42	100
2.	—	0	—	6	17.10	3.59	100
3.	1 grm. hexa.	0	—	6	16.97	3.56	99.36
4.	1 grm. hexa.	0	—	6	18.68	5.17	100.19
5.	3 cc. 40 per cent CH ₂ O	0	—	6	17.00	2.52	106.92
6.	3 cc. 40 per cent CH ₂ O	0	—	6	18.46	3.70	108.32
7.	3 cc. 40 per cent CH ₂ O	10	5 min.	17	16.40	2.92	99.72
8.	3 cc. 40 per cent CH ₂ O	10	5 min.	17	15.89	2.40	99.50
9.	3 cc. 40 per cent CH ₂ O	10	18 hrs.	17	16.98	3.54	99.50
10.	3 cc. 40 per cent CH ₂ O	10	18 hrs.	17	19.62	3.16	99.51

Water of dilution = 100 cc.

Phenol solution used = 15 cc.

Bromide-bromate solution = 0.09970 N.

Hydrochloric acid = 37 per cent solution.

N/10 ammonia = 28 per cent solution.

Thiosulphate = 0.09825 N.

The addition of ammonia to a phenol solution containing formaldehyde was tried, and the results are given in the table (Expts. 7, 8, 9, and 10). If the unknown phenol solution be made 2N with ammonia and the whole allowed to stand for five minutes, the formaldehyde is transformed over into hexamethylenetetramine or some intermediate non-interfering compound, and the determination of the phenol may be made with speed and accuracy. Allowing the ammonia, formaldehyde, and phenol to remain together in the water solution longer than five minutes, e.g., eighteen hours, before the determination is made does not affect the results, as is shown in Experiments 9 and 10.

This method of determining phenol in the presence of formaldehyde would not hold if a condensing agent had been present previously or if the solution had been treated in a way which tended to form oxybenzyl-alcohol, saligeno-saligenin, &c.

In determining phenol in the presence of hexamethylenetetramine the bleaching of the starch iodide colour by the thiosulphate is slightly retarded by the presence of hexamethylenetetramine, and it is necessary to give a few seconds after the addition of the thiosulphate to allow the blue colour time to disappear.

Conclusions.

1. Phenol in the presence of hexamethylenetetramine may be determined by the method already described for the determination of phenol.

2. Formaldehyde interferes with the volumetric determination of phenol by bromine.

3. The addition of strong ammonia to the phenol-formaldehyde solution forms with the aldehyde, hexamethylenetetramine or some intermediate ammonia-aldehyde product which does not interfere with the quantitative determination of phenol. *Journal of Industrial and Engineering Chemistry*, vi., No. 3.

COLLOIDS.*

COLLOID chemistry is a relatively new field of chemistry and physics, although many of the facts of the subjects, notably the discoveries of Graham, have been on record for a considerable time. It is difficult, however, to give a concise definition of a colloid. There are no general considerations which permit us to tell what are, or what are not, colloids. One must apply a series of tests—a sort of qualitative colloid analysis. Methods have been found, as a matter of fact, that enable us to put almost all classes of substances into the colloidal condition.

The conception of colloids originates from diffusion experiments. Graham, who first investigated quantitatively diffusion phenomena, found that while many substances migrated rapidly, others such as glue, gelatin, silicic acid, tannin, aluminium hydroxide, the gums, and albumins migrated very slowly, if at all. He attempted to distinguish between the two groups by methods other than this simple diffusion experiment. In this connection he designed the gelatin jelly test. Above a 2 per cent gelatin jelly in a test-tube he placed the solutions, and he observed the rates of diffusion downward into the jelly. He further modified this test by putting a parchment membrane or other animal tissue between the two layers. He found that those substances that diffused rapidly went through the membrane, while those that did not diffuse were held back. This is the phenomenon of dialysis. Graham here made the first generalisation; the diffusing substances he called crystalloids, the non-diffusing substances he called colloids. He defined a colloid, then, as something in solution which did not diffuse, and did not dialyse.

But this definition is not sufficient. Are colloids coarse precipitates, or are they molecular solutions? This point was never settled. Modern colloid chemistry believes it better to consider what is common to all classes. There is no sharp line of demarcation between them; they are all transitions. There is a continuous series of conditions and phenomena. Let us call the whole group "dispersed systems,"—a system in which the properties change continuously. And we will divide this group into three sub-groups, which division, however, is entirely arbitrary. It has been found practical to use 0.1μ (approximately the limit of microscopic visibility) to distinguish between precipitates and colloids. This limit has been chosen because suspensions of particles of diameter 0.1μ are stable, and do not settle. The pores of fine filter-paper are 1μ in diameter, so one can use filtering as a rough test. The upper limit of the "degree of dispersion" of colloids is approximately the molecular diameter. We have selected as the upper limit $1 \mu\mu$. This then is the answer of colloid chemistry to the question, What is a colloid? It is a dispersed system in which the particles range in diameter from 100 to $1 \mu\mu$. We may distinguish colloids from solutions by their lack of diffusion, and by dialysis. We may distinguish them from fine precipitates by the filtering test. Also colloids are very stable in the absence of electrolytes. But there is perfect continuity throughout; our demarcations are purely arbitrary.

Since the size of the particle seems to be the important distinguishing characteristic, one would conclude that any substance in the proper degree of dispersion would be a colloid. Quite empirically, experience has shown that this is correct. We have colloids of many numbers and kinds.

There are two methods of making colloids:—(a) starting with molecular solutions and letting them grow—the condensation method; and (b) starting with solids and dividing—the dispersion method. Thus we can get colloidal gold by reducing gold chloride with phenylhydrazine to get blue gold, or with tannin to get red gold. On the other hand we can apply the dispersion method and obtain colloidal tungsten by grinding up the metal mechanically; by the action of light on a gold plate; or by the action of the electric current between metallic electrodes under water. In the condensation method it seems that the size of the particles is a function of the concentration of the molecular solution we start with. This function shows a maximum corresponding to a definite concentration. Thus with very dilute and with very concentrated solutions, the size of the resulting particles is very small.

Until recently only liquids were considered as colloidal solutions. But we see that if it is true that a particular degree of dispersion is the defining condition of a colloid, we ought to have colloids that are not liquids. We should have cases of a solid in a gas, of a solid in another solid, of a solid in a liquid, of a liquid in a liquid (emulsion), of a gas in a liquid (whipped cream, beer foam). Notice in each case we have a dispersing medium which dissolves the other material. Alloys and cast-iron are instances of solids in solids; in cast-iron is found ferrite, graphite, and carbides of iron. We have also the solid solutions of van't Hoff. Glass can assume a red colour due to colloidal gold dispersed in the solid medium, our common ruby glass. In a gaseous medium gold dispersed as the solid, as in smoke, also shows the red colour; in fact gold everywhere can give this colour. In the mineral kingdom these systems also are common. Water may be held in crystals as droplets (coarse), as ultra-microscopic particles, or held as water of crystallisation, the molecular solution. Then we have the case of clouds—a liquid in another gas. The cosmic dusts likewise show very different degrees of dispersion. Only in the case of a gas dissolved in another gas, does this conception of colloid not apply. Thus, this general conception enables us to take into consideration an enormously larger number of systems, most of which science has not yet investigated. Thus the subject of

* From a series of Five Lectures delivered by Dr. Wolfgang Ostwald at the University of Chicago. From the *Chemical Engineer*, xix., No. 4.

foams, fumes, fogs, smokes, all colloidal from this point of view, have hardly been opened up, as yet.

Let us consider from the scientific point of view this special degree of dispersion. Let us consider first, the variation in physical properties with variation in the degree of dispersion. If we examine some particles of carmine under the microscope, we find that they are in continuous motion. If we exclude all influencing conditions, we find that they still move. In fact such suspensions in minerals can be seen which have been in motion for thousands of years. This is called Brownian movement. All kinds of dispersoids show this motion, if the viscosity of the medium is small enough. And the velocity of the motion is greater with increasing smallness of the particles. When we study the nature and cause of these motions, we go into the field of the Kinetic theory. We conclude that these motions are the kinetic movements already assumed for gases.

The diffusing property ought to depend upon the size of the particular substance. Thus Pictet and Lume, working under Ramsay, showed all transitions of diffusion. Taking arsenic trisulphide, and varying the concentration, they obtained a series of precipitates from coarse, which settle quickly, through finer and finer, to real molecular dispersion. The stages may be represented as follows:—(1) settle quickly—coarse; (2) settle same day—microscopic, partly retained on filter; (3) pass filter, invisible under microscope, non-dialysable; (4) finest precipitate—partially dialysable; (5) typical colloid, mostly dialysable; (6) solution—molecular dispersion. Filter-paper pores range in size from 3.3μ to 1.3μ . Colloids have a diameter of 0.1μ . Colloids diffuse through jellies as through water. Highly dispersed colloids go through jellies no matter how fine, if pressure is applied. Very concentrate jellies, such as the copper ferrocyanide semi-permeable membrane, will hold back certain molecules. Thus by this method of ultra-filtration we may fractionate colloidal particles of different sizes.

Next we may consider turbidity. There is the perfectly clear colloidal ferric hydroxide and the visibly turbid colloidal sulphur. There are perfectly clear colloids. But there are methods to detect very small traces of turbidity ordinarily invisible. This is the sun-dust phenomenon, or the Tyndall effect. If we make similar conditions under the objective of the microscope so that we look at right angles to the beam of light, we see little spots of light. We do not see a definite picture as from a reflection process, but only little sources of light which come from diffraction phenomena. The same results can be obtained by ultra-microscopic methods against a dark background, as in the case of a mastic suspension in water. If we investigate molecular dispersion, we find the same result. Extreme instances are sugar and sodium sulphate. In concentrate solutions, these show exactly the same kind of Tyndall cone. We are not astonished that salt solutions, liquid ether, organic liquids in general, show ultra-violet cones when examined through quartz dishes. Tyndall cones are thus seen in diluted salt solutions and in systems like ether; thus there are all degrees of optical dispersion.

Next consider colour. Colourless dispersoids show merely opalescence, against a dark background appearing blue, against a light background appearing yellow. Thus we would expect that colloids might have all colours, which is actually the case. Gold may be red, blue, orange, green; silver may also be any, in fact nearly every colour. Colour is mainly due to the size of the particles. The finest have a yellow to orange colour, larger and larger particles go through changes in this order; red, violet, blue, and green, the latter being the coarsest. In the case of gold we are not to think of the colour of its plane surface but its colour by transmitted light. Faraday found the colour of thin gold to be green, corresponding to fairly coarse particles. The blue particles are smaller, violet yet smaller, then through red to orange, the first being the colour of the most highly dispersed condition possible. The colour of a gold solution with a colourless

anion is brown or orange. Silver shows the same changes. It is blue in thin sheets. Its solutions are faintly yellow. The smaller the size of the particles, the less the colour of the liquid. At the highest dispersion silver salts are practically colourless.

What happens when an electric current is passed through these three kinds of dispersoids? There is conduction—a transport of substance. The ions are the material carriers. They may be charged positively or negatively, or with zero charges, in which latter case the particles move very slowly. The sign of the electric charge is not necessarily constant for any given material.

We can change the sign by additions of other materials or by changing the medium. Silver iodide shows both kinds, depending upon which kind of ion is in excess. By pouring a solution of potassium iodide into one of silver nitrate the colloid is produced positively charged. By pouring the silver nitrate into the potassium iodide the colloid becomes negatively charged. The migration of colloids can be shown very neatly by the aid of filter-paper. Filter-papers are suspended above dishes of colloids with the bottom edge of the paper dipping into the respective solutions. The colloids climb up the paper, or not, with a liquid according to their sign. Cellulose always assumes a negative charge when dipped into water (in fact, if large quantities are used sparks may be produced). Positively charged colloids are precipitated and do not rise in the cellulose, while negatively charged colloids climb with the fluid. It is not to be thought that the amount of colloid material moved by the current is proportional to the chemical equivalents. The phenomenon is rather similar to conduction in gases. Here likewise the path of the migrating ion can be changed by magnetic influences. This is known as the Hall effect. Thus we see that the physical properties of the three groups of dispersoids change steadily and progressively.

The chemical properties are fully as important. Do they change continuously or not? In the case of solubility the following result was noted:—Hulett found that finely-powdered gypsum is about a hundred and twenty times more soluble than crystalline gypsum. This does not refer to the rate of solution, but to the final or absolute solubility. The catalytic effects, represented by the decomposition of hydrogen peroxide by platinum black, depend upon the size of the particles. Colloidal platinum in exceedingly small amount decomposes the peroxide. Such effects are produced by "specific surface," that is, the amount of surface in units volume. The increase of surface with decreasing size of particle is a startling and commonly unknown quantity. Consider the following table:—

Edge of cube.		Number of cubes.	Total surface.
1	cm.	1	6 cm. ²
0.1	cm.	10 ³	60 "
0.01	cm.	10 ⁶	600 "
0.001	cm. (diam. of blood corpuscle = 0.0007 cm.)	10 ⁹	6000 "
1	μ (0.0001 cm. = diam of small coccus)	10 ¹²	6 sq. m.
0.1	μ	10 ¹⁵	60 " "
0.01	μ (limit of ultramicroscopic visibility)	10 ¹⁸	600 " "
0.001	μ or 1 $\mu\mu$	10 ²¹	6000 " "
0.1	$\mu\mu$ (diam. molecules)	10 ²⁴	60,000 " "

A platinum plate does not decompose peroxide; a coarse dispersoid does the act better; colloidal platinum does it best of all; solutions not at all.

There are two different kinds of colloids, represented on the one hand by colloidal gold, silver, platinum, &c., on the other by antimony trisulphide, gelatin, silicic acid, aluminium hydroxide, &c. The physical characteristics of the two groups are quite different. In not too concentrated form the colloids of the first class have practically

the same viscosity as water. The viscosity of the second class varies from 0 to infinity (taking water as zero). The viscosity of the colloids of the first class is directly proportional to their concentration. The members of the second class show a sudden break in their viscosity-concentration curves. This is the "setting" point or critical point. This difference must necessarily indicate a change or difference in the aggregation of the molecule. This is explained by the affinity of one of the classes for water. Thus there are two grand divisions of colloids—Suspensions (lyophobic—not liking liquids) and emulsoids (lyophilic—liking liquids). The emulsoids, therefore, have incorporated in them a certain quantity of water in combination. The critical point, it should be said, may be displaced or entirely eliminated by the addition of electrolytes or non-electrolytes.

It is further noted that gelatin solutions and emulsoids in water, in general, secrete a liquid. This secreted liquid is a dilute colloid. Its amount depends upon the acid or electrolyte content, &c. This is syneresis.

Emulsoids absorb liquids. This is shown by the swelling of rubber in benzol and the swelling of gelatin in moist air. When a silver chromate precipitate is formed in a gelatin medium, instead of a continuous layer being formed, the precipitation takes place intermittently in the form of concentric circles.

When water is secreted from the colloid, it may coagulate. This can be brought about by mixing two colloids of opposite electrical charges, or by shaking, so that air particles become intimately mixed with the colloids. The higher in valence the colloid is, the quicker and easier the coagulation is effected. By the same process two colloids may absorb each other. Usually you obtain in this manner a particle which must be at least the size of two colloids. Under these conditions a precipitate is formed, and the reaction is quantitative.

Applications of Colloid Chemistry.

(a) *To Other Sciences.*—The methods used to prevent the passing of fine precipitates (colloids) through filter-paper in analyses are adaptations of the principles of colloid chemistry. The precipitated material may be allowed to stand so that small particles may grow into larger ones; the solution may be boiled to get coagulation of the suspensions; or the solution may be shaken with salts. The use of colour reactions of metal colloids such as gold colloid, to show presence of small amounts of metal, is another application. The intensity of the colloid colour often is greater than that of aniline dyes. This permits of detection of very small traces of the metals. In the case of gold, a borax "pearl" will show the presence of 0.002 millionths of a mgrm., while the spectroscopic will show but 0.12 millionths of a mgrm. The sensitiveness of the colloidal and spectroscopic silver tests is in the same ratio. The colour reactions of metal colloids may be widely applied. Natural money gives a yellow silver colloid, which the artificial does not give. There is an essential oil in the natural product which is the reducing agent, and which has not yet been introduced into the artificial product. Humic acid can be detected in peat by the use of the gold test.

In photography, it has been assumed that the latent image is due to reduction of the silver halide to subhalides (three in number, to account for the varieties of colours obtained in developing). It is now found that the substance is composed of silver halide with metallic silver in the colloidal state. The different colours result from the different degrees of dispersions of the colloid. Red, green, blue, brown colours can be obtained if colloid silver is added in different amounts. The products appear as coloured crystals. Hence crystallisation does not always mean that we get a pure substance.

Many compounds are absorption substances. All the slippery, slimy, gluey substances which will not crystallise, which have no sharp melting or boiling-point, show the typical properties of colloids. A special kind of dispersoid

is the system isoprene-indiarubber. In the process of polymerisation we see the isoprene get viscous. At first the polymerisation product can be dissolved out with absolute alcohol. Afterwards it gets more and more like rubber, and is a colloid. The first phase is a mixture of iso-colloids or iso-dispersoids. Plastic sulphur exists in two allotropic modifications likewise. So with the iso-colloids, as isoprene goes over to rubber. These are sometimes called allo-colloids.

Many of the organic dyes are colloids and this certainly affects their properties. For example, the sulphur dyes show colour changes as functions of temperature. If metal colloids may change colour this way, the idea is justified that the dye colour changes may be due to changes in their colloidal state.

Many crystals are colloidal, as shown by the ultra microscope.

Colloids obey the same law of density (La Place) as the air. In this way the number of molecules in 1 gm. of gas can be calculated and so Avogadro's law proved.

Cosmic dust is supposed to play a large part in the origin of worlds. Movement of the dust by light pressure is the first step in this evolution, and is influenced by the size of the particles. The greatest speed is with particles 10 to 100 μ in diameter. These are typical colloid dimensions.

Many minerals are representative types of colloids. For example, while ordinary rock salt is colourless, a blue variety is known. The blue colour is due to the presence of colloidal sodium, produced probably by the radio-active influence of potassium compounds.

There is a series of silica minerals of practically the same composition, except for water—pure quartz, chalcedony, opal, &c. This whole series of minerals parallels a series of dispersoids of greater or less degree of dispersion. Quartz is supposed to be insoluble in KOH; chalcedony is easily soluble. If, however, quartz is very finely ground, so as to get greater degree of dispersion, KOH dissolves it. Silica dissolves to the extent of 1.6 per cent under ordinary conditions, but if ground to pass a 5 μ sieve, 10 per cent will dissolve.

Soil is a conglomeration of colloids of varying degree of dispersion. Soil physics is colloid chemistry.

A very large application of colloid chemistry is made in the biological sciences and in medicine. Human beings consist mostly of colloids. Protoplasm and albumins likewise are such. Living cells show the Brownian movements. When cells are killed coagulation occurs. Histology deals with colloid chemistry. Water absorption accounts for many of the phenomena of cell history. Likewise muscle movement may be explained on the colloid basis. The colloid metals are used in therapeutics. Colloidal silver in the state of silver nitrate is used in the eyes. Colloidal sulphur is used in skin diseases, colloidal calomel in syphilis, colloidal gold in cancer, and the very latest is colloidal palladous hydroxide in obesity treatment.

(b) *To Industries.*—Colloids are quite generally distributed. For example, wood wool, silk cotton, the dyes (indigo and the blacks), leather (tanning), soap (washing), coffee—all are colloids. Two dyes may be chemically identical, yet have entirely different hues. Two clays, chemically the same, so far as analysis can tell, make entirely different bricks. It is only natural, considering the newness of colloid conception, that many applications at present consist merely in the recognition that colloids exist in the particular instance. Colloid chemistry is young and in many branches this first step of recognition is the only one made. Real scientific application is just beginning.

Many observations have been made, however, since ancient times. In the manufacture of soap, salting out and coagulation have been practised for many ages. In indiarubber, which shows the baffling cases of vulcanisation, one of the first steps is probably absorption. Acheson working with graphite found that increasing the degree of dispersion until the colloidal state is reached

increases the lubricating properties to a most remarkable extent. An important problem in this connection was to find a way to protect the colloid against precipitation by electrolytes. Acheson, following the biblical method of the Egyptians who used a decoction of straw in the manufacture of bricks, used tannin as a protecting material. The explanation is that the emulsoid forms a film about the colloid, keeping each particle shielded from foreign influence. Ruby glass, many precious stones, and ultramarine are colloids.

The behaviour of the hydraulic substances such as mortars, cements, &c., have been explained on the basis of a "hydraulic" theory. This theory offers no explanation of shrinking, elasticity, or hardness. All these properties can be explained on a colloid bases, and the ultramicroscope substantiates this. In the manufacture of clay pottery, colloidal aluminium hydroxide plays a very important part. To this is due the property of plasticity. How to gain this plasticity for moulding and yet have less water to dry out afterwards is a new art. The material may be made so thin as to be cast, all the while having less water than the stiff clays which may be cut with a knife. Some of the finest china is cast this way. The viscosity of the paste is decreased enormously by the addition of a small amount of alkali. At one particular concentration of the alkali we get a permanent suspension of the clay. Greater or smaller concentrations do not serve. This phenomenon of increasing the degree of dispersion is called peptonisation.

A most important and interesting application is in metallurgy. In the carbon-iron series of alloys we have a typical colloid system; the degree of dispersion changes from coarse, in pig-iron, where we have the big microscopic crystals, through the finer grades as in common, annealed, and carbon steels, to the molecular dispersion of the solid solutions. All grades of austenite are so called solid solutions in the iron; martensite is a molecular solution of carbon in iron; pearlite is a more coarse suspension of carbide in iron. Characteristic structures which come between the two extremes, which are neither one nor the other, are osmondite and sorbite; they are peculiar to the tempered steels and show maxima of properties; the dispersion is just that of colloidal size. In the making of the best steels, therefore, the aim is to make colloids.

There are industries which we must call colloid industries, because they have been so from the beginning, and handle only colloids. The cellulose industries are of this sort—paper-making, the manufacture of parchment paper, mercerising cotton, and the manufacture of artificial silk.

All the processes used to make celluloid, and plastic masses like bakelite, and those processes starting with casein, are colloid industries. Celluloid is a solid solution, containing camphor; bakelite is an isocolloid, a polymerisation of phenol and formaldehyde with alkali. Other colloid industries are the indiarubber industry, which in both the coagulation and vulcanisation processes presents a fertile field for the application of colloid ideas; also the manufacture of starch and glue. In the sugar industry, the problem is to obtain all the sugar from the molasses. Cooking processes are largely colloidal, not only in the case of jellies, jams, and gelatins, but in other operations, such as the cooking of steak, where the problem is to form a coagulated layer over the outside quickly to retain the juices. The ageing of bread is another instance of syneresis. The precipitation of solids from smoke and dust by the famous Cottrell process is a typical colloid reaction.

If one asks how it is that there can be a brand new science of such a wide application, how it is that only recently the colloid idea has appeared as of universal extent and supreme importance, the answer is that science in general has occupied itself with two big classes of materials. Matter has been studied either in bulk or in molecular solution. Very much has been learned about

these two conditions, at the same time neglecting a whole world of dimensions in between. Because we can conceive of converting everything into these dimensions it is to be expected that the new science will have such a wide application.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

PRIMITIVE OCEANS AND CONTINENTS.

M. Emile Belot has already shown how the translation of the earth into its original nebula gave to its atmosphere a circulation that caused the Antarctic to receive the first of all the deluges. Applying this theory to volatile bodies other than water, M. Emile Belot established the fact that the sea salt must have been deposited on to the Antarctic zone before the water, so that the first oceans were very strong in salt; it is this concentration of salt outside the continental areas that enabled vegetation to take place from the very beginning of the primary era. The continents, and notably their archæan moles, have always the seas as antipodes. The weight of the oceans is equal to the weight of the land raised on the base level of 2500, which is the primitive level of the terrestrial anhydrous nucleus.

CHEMICAL CONSTITUTION OF CELLULES.

For several months past MM. George Mayer and André Scheffer, assistant at the physiological laboratory of Prof. Dastre, at the Sorbonne, have been studying the chemical constitution of cellulose and of organs, especially considering the phosphorated lipidic substances and cholesterol. They have deduced some interesting observations concerning the movement of water in the organism. They have likewise noticed that the parenchymatous organs, the noble organs, such as the liver and the spleen, had a constant concentration in cholesteroline and phosphorated substances. MM. Mayer and Scheffer have wondered if the same thing was true for the whole organism. Their conclusion is that for an organism of a determined species there is constancy of the phosphorated substances and of the cholesteroline.

VISION AT A DISTANCE.

For a long time many physicists have been seeking to solve the marvellous problem of sight at a distance. Science has already realised so many admirable conquests, such as wireless telegraphy and telephony and coloured photography, that the discovery of television no longer seems an impossible dream. At the same time as Prof. Ruhner in Berlin, M. Eduard Belin in Paris, and M. George Rigoux in La Rochelle, made some years ago some rudimentary experiments of television, which experiments were not without a certain interest. These researches have just become more precise. In an important communication made to the Academy of Sciences by Prof. Gabriel Lippmann, this learned physicist explained the recent improvements made in the apparatus of television invented by M. Georges Rigoux, to which he has given the name of *Telephote*. As the telephone transmits by wires sonorous variations of scales of sounds, the telephote transmits luminous scales of the variations of shade and light. The telephote with two wires, without counting the wire of synchronism uniting the transmitting apparatus to the receptive apparatus, rests on the following principles:—A parabolic or a concave mirror projects the sheaf or cone of a Nernst lamp of 2000 candles on an object of which the image is required to be transmitted. Each point of the object thus lighted up is projected by a lens on a plate or tablet formed of sixty-four cellulose of selenium. We know the curious property of this metal, the electric resistance of which varies proportionally with the intensity of the light to which it is subjected. It is this

property of selenium that is utilised in the telephoto. By means of these sixty-four cellules, it is possible to transmit a considerable number of figures or combinations of signs. This plate of selenium cellules is crossed by an electric current proceeding from a dynamo. Each cellule, according to whether it is or is not lighted, will then send an electro-magnetic relay, a simple ringing relay, a current that will attract a palette or leave it immovable. Thus a whole series of electric currents will start from electro-magnetic relays corresponding to the cellules of selenium lighted up by the luminous points of the object the image of which is to be transmitted to a distance. These currents arrive on a collector of rapid rotation, revolving at the rate of 450 turns a minute. This collector sends on to the line wire all the currents collected. At the receiving post these electrical variations are received in a coil of magnetic rotatory polarisation the axis of which is lighted by an electric arc. The successive currents will turn the plane of polarisation of light. Thus for each current corresponding to a luminous point of the object a cone of light will be produced which will pass through the nicols, and which, after having passed through a lens and a purifying screen, will fall on to a revolving mirror formed by eight little mirrors. These mirrors will reflect on to a screen the image of the objects situated at the transmitting station. M. Georges Rigoux has succeeded with the help of the telephoto to transmit into his laboratory the image of the letters of the alphabet. M. Lippmann has shown a whole photographic series of the letters T, U, L, &c., formed each of a series of little luminous lines, and to obtain an image nearer to reality, only a little more misty. Up till now, M. Georges Rignoux has not yet tried to transmit the half lights, but that is an improvement that may be easily realised. To obtain the image of a person, it will be necessary to employ a tableau or plate of from 3000 to 4000 cellules of selenium. This young physicist of La Rochelle also foresees the suppression of the screen at the arrival. Thus there will be formed an aerial image that will be much more luminous and much more distinct.

RABIC VIRUS AND SERPENTS.

M. Edmond Perrier, Director of the Paris Natural History Museum, has communicated to the Academy a new note from M^{me}. Phisalix, concerning the action of rabic virus on batrachians and serpents. The savants who have made a study of rabies admit without further inquiry that all cold-blooded animals are refractory to this madness; but the fact up till now has been demonstrated only for the frog, for some fish, and the Mauretanian tortoise (Reinlinger). M^{me}. Phisalix has inoculated some rabic virus to our different species of frogs, to the common toad, to the land salamander, to the slow worm, to adders (the viperine adder and the collared adder), and lastly to the asp viper. She has seen that the result was distinctly negative for the greater part of these species, although for three series of animals out of ten, she had taken the precaution to make them live in a vapour bath of 35° C., about equal to that of vertebrates with hot blood. But vipers and salamanders (the experiments concerned forty-eight subjects of the first species and twenty-two of the second) were continually dying paralysed, with a survivance of 5 to 8 days for the vipers and 6 to 12 days for the salamanders. The duration of this survivance was independent of the place of inoculation; it is thus that the vipers that had received the fixed virus in the eye did not die any sooner than those that had received it under their skin. These vipers, possibly mad, were, however, only paralysed in the muscles of their bodies, for they could bite in erecting their venomous stings if they were strongly excited, but they were quite unable to put themselves into a position of defence and to unbend quickly as they generally do. Their brain, inoculated in the same way, to normal vipers, made these latter die with the same symptoms and in the same lapse of time as the fixed virus. The experiment was continued as far as the fifth passage both for the vipers and for the salamanders.

Now, did these vipers and salamanders die of rabies? To make sure of the matter, M^{me}. Phisalix made one of the trials that assure an absolute certainty, the one that Pasteur and Roux gave in 1881, the inoculation to the rabbit, of the suspected product, under the meninges; so then some trepanned rabbits received the cerebral pulp of the vipers and salamanders that had died after the inoculation of the fixed virus; these rabbits all resisted, and moreover were not proof against the fixed virus. So then vipers and salamanders did not die from rabies. Were they sensible to the non-rabic nervous substance? That is what has been confirmed by the experiment: "The normal cerebral substance of the rabbit, or that of their own species, is a poison for the viper and the salamander, whilst it has no noxious action on the other animals inoculated, toads, frogs, slow-worms, and adders." The exception presented by the viper and the salamander to the resistance to the rabic virus is then only apparent, and experiments are at present being made to try and discover what is the mechanism of the immunity.

THE SUN IS A STAR OF THE MAGNITUDE - 26.5.

The classification of the stars by order of magnitude, by taking as a basis their apparent brilliancy, was not at first done with great strictness; it results that stars considered as being of the second magnitude when they have been studied by means of the improved methods and instruments that can now be employed, have been discovered to be more brilliant than others of the first magnitude. Thus, Aldebaran, formerly classed among stars of the first magnitude, shines considerably less than Sirius. The brilliancy of this latter star, the most brilliant of all, being taken as equal to that of 1000. Laugier, by a photometrical method due to Arago, has discovered that the luminous intensity of Aldebaran was expressed by the figures 220. Such facts have led to the modification of the first classifications on several points. To-day, a star of the first magnitude is twice and a-half times more brilliant than a star of the second magnitude; a star of second magnitude shines two and a-half times more than one of third; and so on. Stars that shine two and a-half times more than one of first magnitude are called stars of 0 magnitude; those that give a light two and a-half times more intense than these latter belong to the magnitude -1, &c. Prof. Ceruski has recently undertaken to determine the order of the sun's magnitude by taking this rule as a basis. In operating according to different methods, he has obtained very concordant results, according to which the great luminary is a star of the magnitude -26.5. This is equal to saying that the sun sends us as much light as 880 millions of stars of first magnitude.

CORRESPONDENCE.

MELTING-POINT OF CANE SUGAR.

To the Editor of the Chemical News.

SIR,—It may interest some of your readers to learn that the melting point of cane-sugar is 185° C., and not 160° as given in the text-books. I made this discovery in March of the present year. It is curious that, in the case of so common a substance, such a mistake should not have been earlier rectified. The correction may already have been made, but I can find no record of it.

My observations were taken with various samples of sugar intended for domestic use. With specially purified sugar the melting point may possibly rise to 186°.

While in Heidelberg during last Easter vacation, I happened to mention the correction to a Professor of Chemistry there. It may be that he has already made it known through the medium of one or other of the German chemical journals.—I am, &c.

B. BURNE, M.A., Ph.D.

23, Henry Street, Redcar, Yorkshire,
July 19, 1914.

NOTICES OF BOOKS.

Brennereifragen. ("Distillery Questions"). By D. SIDERSKY. Braunschweig: Friedrich Vieweg und Sohn, 1914. (M. 1.60).

THIS book contains two articles on recent advances in the manufacture of spirit, which give an outline of the results of the author's personal experience. The first deals with methods of continuous fermentation, and also describes the microscopic control of the process, and the second article gives details of the new distillation and rectification apparatus which has been adopted in the most modern distilleries. It has been found that purely physical methods of rectifying the raw spirit are most satisfactory, and the new processes show very clearly the good results obtained when technical practice is based upon scientific investigation.

The Elements of Chemistry. By H. LL. BASSETT, B.A., B.Sc. London: Crosby Lockwood and Sons. 1914.

CANDIDATES for the Conjoint Board and the various First Medical Examinations will find that this book contains all the chemistry that they require, and the advantages of being able to use a single book, and one moreover which has been written specially for them, are obvious. It begins with a section on general or theoretical chemistry, in which the laws of the science, the fundamental conceptions, and the Periodic System are discussed. The next section describes the preparation and properties of the elements, taken in the order of their positions in the periodic table, and their important compounds. Then Organic Chemistry is similarly treated, and the final chapters are devoted to practical work, including easy qualitative and some elementary quantitative analysis. The treatment of the subject is very concise and systematic, but hardly inspiring; the book is more suited for students who are getting up chemistry for an examination than for general school use, and for beginners it would be absolutely essential to make some alteration in the order in which the subject was presented.

The Gas Chemists' Summary. 1913. By A. V. HENDRICKSON. London: Walter King. 1914.

THIS is a really useful little book for gas chemists, and an annual edition of it would be a boon to busy men who have not always time enough to spare for a thorough study of periodical literature, without which it is practically impossible to keep up to date. A review is given of all the papers published during 1913, and containing matter which is of interest to gas chemists. Modifications of processes, fresh methods of analysis, and many new results are included, and usually full details and not merely short summaries are given. The classification adopted appears to be on the whole the best, and the author has divided his space judiciously among the different subjects. Articles in foreign as well as those in English periodicals have been abstracted, and a good index is provided.

Robert Boyle: A Biography. By FLORA MASSON. London: Constable and Co., Ltd. 1914.

THIS biography of Robert Boyle is a pleasantly written account of the lives of the great philosopher and his family. For readers of scientific tastes one of the chief interests of the book will lie in its descriptions of the meetings of the "Invisible College," the embryo of the Royal Society, the Oxford branch of which met in Boyle's rooms, and of the early meetings of the Royal Society itself. Boyle's scientific and philosophical work is discussed, and a charming picture is given of the man himself, of his busy life passed in tranquillity and simplicity, and of the multitude of friends who were attracted by his great reputation and gathered round him to listen to his views and to discuss scientific subjects.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 21, May 25, 1914.

Oxidation of Copper: Influence of Temperature and Pressure.—Ernest Berger.—The oxidation of copper by dry oxygen takes place at any temperature, at any rate up to 15°. The rate is practically tripled for an interval of 10°. The rate seems to be directly connected with the pressure of the gaseous layer condensed at the surface of the metal.

Organic Uranium Salts. G. Courtois.—By the action of pure uranic monohydrate upon the corresponding acid the author has prepared the formate, acetate, propionate, butyrate, isobutyrate, valerianate, and isovalerianate of uranyl. All these salts except the first contain two molecules of water and form a very homogeneous group. They can easily be dehydrated to give the corresponding anhydrous salt. They are all soluble in water, and their saturated aqueous solutions are decomposed by sunlight.

Hydrogenation of Cyclic Hydrocarbons by Sodammonium. Preparation of Naphthalene Tetrahydride.—P. Lebeau and M. Picon.—Sodammonium can be used to hydrogenate naphthalene, giving 9-10ths of the theoretical yield of the 1.2.3.4-tetrahydride. Its boiling-point is 208°, which is rather higher than that attributed by Leroux to the hydrocarbon obtained by the action of hydrogen on naphthalene in presence of reduced nickel. The hydrogenation is accompanied by the formation of sodamide, and the reaction can be represented by the equation $C_{10}H_8 + 4NH_3Na = C_{10}H_{12} + 4NH_2Na$.

Bulletin de la Société Chimique de France.

Vol. xv.-xvi., No. 11, 1914.

Heats of Formation of Hydrates of Carbonylferrocyanides.—J. A. Muller.—The author has prepared the sodium, potassium, strontium, and barium salts of carbonylferrohydrocyanic acid, and has determined the heat of combination of the anhydrous salts with liquid water. The results are as follows:—

$Na_3FeCO(CN)_5 \cdot 7H_2O$		12.3 cal.
$K_3FeCO(CN)_5 \cdot 3.5H_2O$		5.7 "
$Sr_3[FeCO(CN)_5]_2 \cdot 4H_2O$		7.5 "
$Ba_3[FeCO(CN)_5]_2 \cdot 11H_2O$		23.8 "

Action of Acids on Diphenylnitrosamine in Hydroalcoholic Solution.—M. Marquoyrol and H. Muraour.—Diphenylnitrosamine is very readily hydrolysed by strong acids. The first action is to regenerate diphenylamine, nitrous acid or ethyl nitrite being formed. The action, however, does not stop at this point, and after some hours a precipitate of the dinitroso derivative of diphenylbenzidine is obtained. A small quantity of the mononitroso compound is also formed.

MISCELLANEOUS.

Researches on the Alteration of Milk containing Bichromate.—André Kling, M. Gelin, and M. Lassieur.—The authors find that potassium bichromate, although it may not be the ideal preservative, furnishes better results than any other. The quantity employed may be increased to three times the usual dose without any fear of causing oxidation, even at a relatively high temperature. It must not be forgotten, however, that it does not appreciably diminish the alteration of milk but merely enables an analysis to be performed owing to the fact that it retards curdling.—*Annales des Falsifications*, No. 67, 1914.

THE CHEMICAL NEWS.

VOL. CX., No. 2853.

SIMPLE METHODS FOR THE DETERMINATION OF DISSOLVED OXYGEN IN WATERS, EFFLUENTS, &c.

By PERCY KAY, Ph.D.

THE estimation of free oxygen in waters by methods other than the gasometric has been investigated by many chemists—Dupré and Dibdin (*Analyst*, x., 156), also Roscoe and Lunt, who employ the method of Schützenberger. The method doubtless gives good results, but the apparatus is somewhat intricate and involved. The following methods are based on the oxidation of certain salts in alkaline solution by dissolved oxygen, notably those of iron and manganese.

METHOD A.—By means of Ferrous Sulphate.

Bottles of varying capacity, 12 oz. to 20 oz., were almost completely filled with the water to be examined. A weighed quantity (1 grm.) of ferrous sulphate acid, then about 2–3 grms. solid caustic potash or soda, and the cork inserted, care being taken that the bottle was completely full.

After occasional agitation during a period of two hours, the dark bluish green precipitate is emptied into a dish, acidified with sulphuric acid, and the excess of iron found by titration with permanganate.

Example.—342 cc. of water (12 ozs.) were taken, 1 grm. ferrous sulphate and caustic potash added. After two hours absorption the contents were acidified with sulphuric acid and titrated with N/10 KMnO₄, of which 33 cc. were required. The ferrous sulphate alone required 37.5 cc. N/10 KMnO₄. Hence 37.5–33=4.5 cc. for oxygen in water examined. Since 1 cc. N/10 KMnO₄=0.56 cc. O, this is equivalent to—

$$\frac{4.5 \times 0.56 \times 1000}{342} = 7.34 \text{ cc. per litre.}$$

Capacity of bottle.	Cc. KMnO ₄ .	Oxygen.	Cc. oxygen per litre.
376	5	2.80	7.4
342	4.5	2.52	7.34
580	8.6	4.8	8.25
580	8.0	4.5	7.76
580	7.6	4.25	7.33
342	4.6	2.6	7.60

Mean 7.6

METHOD B.—By Manganese Sulphate.

The method of procedure was similar to Method A, but about 1 grm. manganese was added, followed by caustic soda or potash, together with a few crystals of potassium iodide. The resulting hydrated oxide of manganese determined by the amount of iodine set free on acidification.

Example.—342 cc. bottle was filled with the water, about 1 grm. MnSO₄ added, then a few pieces of caustic potash and a few crystals of KI. The whole was allowed to stand two hours, and then poured into a porcelain dish, acidified with HCl, and the liberated iodine determined by N/10 thiosulphate, 4.5 cc. of which were required. Hence—

$$\frac{4.5 \times 0.56 \times 1000}{342} = 7.35 \text{ cc. per litre.}$$

In this method only one titration is necessary. The iodine liberated by the action of the oxide of manganese on the potassium iodide is a measure of the oxygen present, 1 cc. N/10 Na₂S₂O₃ = 0.56 cc. oxygen. In this way the

cc. per litre of oxygen found, using bottles of varying capacity, were:—

$$\begin{array}{r} 7.46 \\ 7.26 \\ 7.35 \end{array} \left. \vphantom{\begin{array}{r} 7.46 \\ 7.26 \\ 7.35 \end{array}} \right\} 7.36 \text{ mean.}$$

Ordinary medicine bottles of white glass were used throughout, and the results were sufficiently concordant. The same water by gasometric methods contained 7.42 cc. oxygen at 15° C. I believe that the amount of oxygen dissolved in fully aerated water to be 7.86 cc. at 10° C. per litre as Winkler has found. The coefficient absorption as hitherto employed, based on Bunsen's work, appears to be too low.

Winkler (*Ber.*, xxiv., 3608) gives the coefficient as follows:—

$$0.0489 - 0.001341 t + 0.0000283 t^2.$$

I am aware that methods similar to the above have been advocated, but none hitherto published are so simple while at the same time possessing a considerable degree of accuracy. The oxygen dissolved in waters is to some extent a criterion for the purity of the water, hence some ready method for its determination appeared to be desirable.

5, Roseville Road, Harrogate,
July 20, 1914.

ACTION OF BROMINE ON HYDROXIDES OF LANTHANUM AND THE DIDYMIUMS.

By PHILIP E. BROWNING.

IN 1909 Roberts and I (*Zeit. Angew. Chem.*, lxiv., 302; *Am. Journ. Sci.*, xxix., 45) showed that by treating with bromine the hydroxides of the earths of the ceric group in suspension in a dilute solution of potash or soda all the earths dissolve except the ceric oxide.

We observed that the hydroxides free from cerium dissolve in the solution of bromine at unequal rates (Hauser and Worth observed a similar action when they treated the ceric earths with chlorine and hydrogen peroxide, *Zeit. Anal. Chem.*, xlviii., 679), and the velocity is greatest in the case of lanthanum.

I proposed to base upon this property a method of separating lanthanum from the didymiums.

To determine the progress of the separations I made three typical solutions of neodymium containing respectively the following quantities of oxide in the same volume (20 cc.) of water:—

No. 1.	0.25 grm.
No. 2.	0.05 "
No. 3.	0.01 "

These typical solutions were examined by the spectro-scope using the same thickness (3 cm.) as well as the solutions the absorption spectrum of which was compared with theirs. The spectrum of the third typical solution was hardly visible, and the spectrum of neodymium could not be seen in the conditions of the experiment with solutions of lower concentration.

A first mixture of ceric earths, free from cerium, the spectrum of which corresponded with that of the typical solution No. 1, was treated with bromine water. The filtered liquors, rich in lanthanum, showed the neodymium spectrum plainly. This liquor was precipitated with oxalic acid, and the oxalates were transformed into oxides by calcination; 0.5 grm. of these oxides dissolved in 20 cc., and examined with a thickness of 3 cm. gave a neodymium spectrum corresponding to the typical solution No. 2.

A second similar treatment of the oxides gave a product still richer in lanthanum, the spectrum of which corresponded to that of typical solution No. 3.

When these last oxides were again treated with bromine water the neodymium spectrum was hardly visible in the conditions mentioned above when 0.5 grm. of the product

was submitted to the spectral examination. Magnetic measurements confirmed the spectroscopic observations.

I then compared this new method with that of Auer von Welsbach, in which the double nitrates of the type $M(NO_3)_3 \cdot 2NH_4NO_3 \cdot 4H_2O$ are submitted to fractional crystallisation, and which is at present considered the best for the extraction of lanthanum. After ten series of fractionations, carried out with ten fractions, the crystals at the head of the series were practically colourless; 0.5 grm. of the corresponding oxides gave, in the experimental conditions described above, a more intense spectrum than that of the typical solution No. 3.

The mixture of ceric earths which I used in the above experiments contained very little praseodymium and very large quantities of lanthanum and neodymium.

I repeated these various experiments with earths very rich in praseodymium. In this case also, after three treatments with bromine, I obtained lanthanums less rich in praseodymium than by Welsbach's method after ten series of crystallisations.

The quantities of lanthanum obtained in the two cases were comparable relatively with the quantities of raw earths which I started with.

A more searching comparison of these two methods convinced me that if at the beginning of the treatments the bromine method gives incomparably quicker results, in the end that of Welsbach gives better results.—*Comptes Rendus*, clviii., 1679.

THE CHEMICAL SIGNIFICANCE OF CRYSTALLINE FORM.*

By THEODORE W. RICHARDS.

WHEN in 1669 Nicholas Steno discovered that a given crystalline angle possesses always a constant value for any given substance, an important circumstance concerning the chemical significance of crystalline form was established. The discovery has been abundantly verified in recent years, especially by Tutton. A century and a half after Steno the investigation of Mitscherlich added great weight to this significance; for Mitscherlich showed that substances with analogous composition often possess also analogous or even isomorphous crystalline forms. At that time this discovery assisted in fixing various atomic weights by pointing out the probable molecular magnitudes of a number of previously misinterpreted substances; but to-day other knowledge has rendered this office of isomorphism unnecessary. The discovery of Mitscherlich is now much more useful to us as a means of interpreting the crystal forms themselves, assuming the molecular constitution of the molecules, than as a means of fixing atomic weights.

In the intervening years since that early time the aspect of crystallography has greatly changed. Instead of concerning himself merely with the measurement of external angles and the fixation of external zones, the crystallographer has become interested in the fundamental forms of symmetry which determine the arrangement of associated particles in space; and from the investigations of Hessel (1830) and Frankenheim (1835) to those of Barlow at the present time, the new logical system of crystallography has not so much supplanted as it has developed and supplemented the older crude classification. According to this new system of crystallography the interest lies in the arrangement of space-gratings or points distributed symmetrically in three dimensions. These points we must consider as being the centres of the "crystal units" which build up the solid system, and each of these must be supposed to consist of one or more molecules. In our effort to visualise the nature of a crystal on this basis, we

cannot help asking at once two questions: How far does each molecule spread out around the point which marks its centre? What forces hold these points in their relative position towards each other, thus maintaining the rigidity of the solid structure?

In 1901 a theory was advanced which seems to provide a plausible and reasonably satisfactory answer to both these questions, namely, the theory of compressible atoms (Richards, "The Significance of Changing Atomic Volume," *Proc. Am. Acad.*, 1901, xxxvii., 1; 1902, xxxvii., 399; 1902, xxxviii., 293; 1904, xxxix., 581; *Zeit. Phys. Chem.*, 1902, xl., 169, 597; 1903, xlii., 129; 1904, xlix., 15. This theory entirely abandons the old idea of small hard atoms at a distance from one another. It makes no assumption as to just how the "substance" of the atom, whatever that may be, is distributed within the so-called "sphere of influence," but points out the fact that in all the relations in which the volume of the atom is important, the volume of the "sphere of influence" is really the essential thing. The hard particle in the centre, formerly imagined to be far from its neighbour, even in a solid, is purely an abstraction and has no corresponding basis in observed facts. We have really no right to pretend to know how the material is distributed within the "sphere of influence." The material is somewhere within that space, but the outside of the space which the atom reserves for itself acts as if it were something very real, and cannot be considered but as the boundary really to be reckoned with.

The high degree of rigidity, impermeability, and permanence possessed by most solids combine to suggest that the substance of the atom is distributed throughout the whole space, but not necessarily evenly distributed. It may be on the surface of the "sphere of influence," like the material of a hollow rubber ball, or it may be more concentrated towards the middle, gradually decreasing in concentration on the outside; at present we have no means of deciding.

The attitude of mind with regard to the compressible atom involves not merely a difference in nomenclature. The name "sphere of influence" is vague; on the other hand the limit of approach to the centre of an atom is definite, if variable. As used above, "sphere of influence" is used to denote the limit of approach to the atomic centre; but the forces residing in an atom doubtless, at least in part, extend further. Hence to call the space occupied by the atom the real effective volume the atom is to give a definite name to an idea which the phrase "sphere of influence" would describe but vaguely and incorrectly. Faraday's conception of "tubes of force" proved to be a fruitful idea because the conception assisted in visualising the phenomena concerned; and to even a greater extent the idea of the compressible atom helps in this case, partly because the facts themselves are more tangible.

On this basis the atom must be assumed to be compressible, because its boundary shrinks when mechanical pressure is applied, even, apparently, at the absolute zero of temperature (Richards, "Faraday Lecture," *Journ. Chem. Soc.*, 1911, xcix., 1207); and the ascription of compressibility to the atom at once clears up a great variety of facts which would otherwise be difficult to understand. Because of its compressibility, the atom must be supposed to be compressed whenever any external force is applied through the action of either chemical affinity, which draws two atoms powerfully together, or cohesive affinity (a similar but less powerful attracting agency) or outside pressure applied mechanically. In a series of papers it has been shown that many facts previously not comprehensible become conceivable and easily correlated with these premises in mind, and the support which the theory thus receives is so great that it may reasonably be used as a working hypothesis in many directions. The wide scope of this idea was recognised immediately by the author. In the second paper concerning it (1902), many of its bearings were briefly catalogued; and in this list the eighth item

* *Journal of the American Chemical Society*, xxxv., No. 4.

reads as follows:—"It explains all tri-dimensional relations of material, such as stereochemistry and crystal form, at least as well as any other theory ("The Significance of Changing Atomic Volume," *Proc. Am. Acad.*, 1902, xxxvii., 410; *Zeit. Phys. Chem.*, 1902, xl., 608).

The bearing of the idea upon stereochemistry has already been briefly taken up in the Faraday Lecture of 1911 ("Faraday Lecture," *Journ. Chem. Soc.*, 1911, xcix., 1212; *Smithsonian Report for 1911*, p. 210; *Revue Sci.*, 1912, l., 327; *Naturwissenschaftliche Rundschau*, 1911, xxvi., 494; *Science*, 1911, xxxiv., 546); the object of the present paper is to discuss its application to the structure of crystals.

In the intervening time (in 1906) one aspect of the question has been considered by Barlow and Pope (*Journ. Chem. Soc.*, 1906, lxxxix., 1675; 1907, xci., 1150) in a series of elaborate papers. These distinguished investigators entirely agree with and support the conclusion that the "spheres of influence" (or as I prefer to call them, the atoms themselves) must be closely packed in a crystal in order to account for the maintenance and rigidity of the crystal structure. They reject, however, the idea of the compressibility of the atoms, while admitting deformability, and in spite of the fact that at the same time they assume the possibilities of great arbitrary changes of atomic volume under different circumstances (Barlow and Pope, *Journ. Chem. Soc.*, 1906, lxxxix., 1675). They make as their guiding principle the assumption that each valency in a given compound has essentially the same volume, and hence that the atomic volumes of combined elements are directly proportional to their valencies. This is, of course, entirely inconsistent with Kopp's system of molecular atoms, which, although not by any means flawless, seems less arbitrary than the newer idea.

The assumption concerning the so-called valency-volume seems to me to be a very doubtful tenet, not only because there seems to be no reason *why* each valence in a given compound should have the same volume, but also because it leads at times to extraordinary and improbable conclusions. Although probably each atom present affects every other to some extent, I can see no reason why, for example, all the remaining carbon and hydrogen atoms in benzene should nearly double their volume when four atoms of bromine are substituted for hydrogen, as the Barlow-Pope theory demands. (The molal volume of benzene is 77.4, of tetrabrombenzene is 130.2. See Barlow and Pope, *Journ. Chem. Soc.*, 1906, lxxxix., 1679). The argument adduced by these investigators as the most striking in support of their remarkable assumption is the set of data found by Le Bas giving the molecular volumes of the liquids of normal paraffins just above their melting-points. Entirely apart from the question as to whether or not the arbitrary choice of the temperature of comparison really indicates similarity of physical composition, and also apart from the fact that these figures deal with liquids and not with solids, it may be readily shown that the figures cannot possess the significance which Le Bas and Barlow and Pope ascribe to them. These investigators calculate atomic volumes on the assumption that a gram-atom of hydrogen occupies 2.97 cc. and a gram-atom of carbon four times that space, from their assumed premise that the atomic volume depends essentially on the valency. The calculated values for the molecular volumes of the hydrocarbons obtained by adding the corresponding multiples of these figures agree closely with the facts, it is true; but so would values calculated on almost any other assumptions within reason. This is because the higher paraffin hydrocarbons having the formula $C_n H_{2n+4}$ approach closely the composition of the hydrocarbons $C_n H_{2n}$ when n is large; in other words any ratio between carbon and hydrogen which fits one hydrocarbon will fit almost as well another. To illustrate this, it is only necessary to repeat extracts taken at random from the table of Le Bas, giving not only the observed molecular volumes and those calculated on the assumption of Barlow and Pope ($H = 2.97$ and $C = 11.88$ cc.) but also

another column calculated on an entirely different basis, for example, $H = 4.42$ and $C = 8.84$ cc.

Formula of compounds.	Observed molecular volume.	Pope and Barlow calculated vol. C=4 vol. H.	New assumption vol. C=2 vol. H.
$C_{11}H_{24}$	201.4	202.0	203.3
$C_{20}H_{42}$	362.5	362.3	362.3
$C_{27}H_{56}$	487.4	487.1	486.2
$C_{35}H_{72}$	629.5	629.6	627.6

It will be noticed that the new figures, calculated on an entirely different basis, correspond almost as well with the observed figures as those calculated by Pope and Barlow. The greatest difference between fact and theory is less than 1 per cent, and the average difference is less than 0.4 per cent.

When account is taken of the fact that the densities which afford the basis for these molecular volumes depend upon the temperature chosen for the determination, and that the really legitimate temperature for such a comparison is unknown, the agreement shown by the figures in the middle columns seems even less convincing. The average deviation from the facts shown by the figures in the last column corresponds to a difference in temperature of only about 5°, and the true temperature for comparison is certainly not known within that amount. Therefore the last row of figures does not deviate more from the observed quantities than by an amount which may be due simply to the arbitrary temperatures chosen for comparison. In short, as an argument in support of the constancy of the valency-volume in any one substance, the table of molecular volumes of hydrocarbons has no significance.

Some of the other arguments advanced in favour of the approximate equality of the valency-volumes seem to me in the same way to be equally good arguments in favour of almost any other reasonable theory which involves close packing of molecules. On the other hand, the Barlow-Pope theory in its unmodified form fails to account either for the varying angles of some truly isomorphous substances, or for the distortions observable in some of the less symmetrical forms. Moreover, there are other facts shortly to be pointed out which militate gravely against the theory. In brief, I can find no fact brought forward in support of the valency-volume idea which is not equally capable of supporting the theory to be elucidated in the following pages; but on the other hand I can find many facts beyond the reach of the former and explicable with the help of the latter theory.

While greatly regretting the need of thus pointing out the lack of cogency in some of the arguments adduced by these eminent investigators, I take pleasure in expressing my appreciation of their valuable work in collecting and collating a great variety of crystallographic details.

Let us now develop the somewhat differing line of argument presented by the theory of compressible atoms. This theory maintains that the atoms (or the spheres of influence which represent the atoms in their outward relations) are compressible, and the space occupied by each atom is determined by the varying pressures exerted upon it by other atoms in its neighbourhood, as well as by outside pressure. It is clear then, that being pressed upon in different ways on different sides, the atoms must become not only diminished in volume but also distorted in shape. Clearly, one may conceive that a molecule built up from such distorted shapes would itself be complex in its outer form, and that this complexity might well be the determining factor in deciding the shape of the crystal aggregate when many similar irregular molecules were packed together. Moreover, because not only the atoms, but also the molecules consisting of aggregates of atoms, are to be looked upon as compressible, there is considerable flexibility in this matter of fitting together the imaginary analogous shapes. If we grant the attribute of compressibility, there is nothing at all singular in the

fact that although caesium sulphate possesses a larger molal volume than potassium sulphate, its crystal form is not very different. We have only to imagine that in these two substances the arrangement of the atoms is similar, and that the mode of their fitting together is such as to allow the difference in volume wherever it appears to be in part taken up by a re-adjustment of the internal compressions of different parts of this molecule. The same argument applies to the case of benzene and its tetrabrom substitution product. Moreover, we must remember that the doubling of the bulk of a solid increases its diameter by only about 26 per cent; thus considerable changes might not show greatly in the crystal angle. Similarity in crystalline form in such cases does not necessarily prove, as others have thought, that the theory of valency-volume is the best theory.

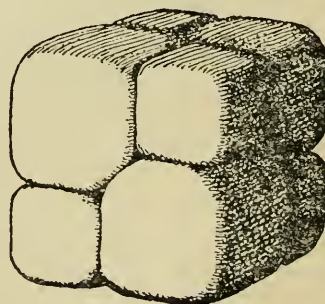
In seeking to apply the theory of compressible atoms to the facts of crystallography, one is struck at once by the obvious difficulty of attacking with any known variety of mathematics a situation so complex; for the theory assumes a system composed of units of varying compressibility, not only as regards one another but also as regards different parts of the same atom, and also the existence therein of many varying internal attractive forces, each tending to produce a different degree of compression. The necessary complication is no argument against this theory, however; nature often presents complicated phenomena which are due to the simultaneous action of simple laws. For example, the apparent path of Halley's comet in the heavens was highly irregular, but it was made of very simple factors. Again, nature does not hesitate to allow three or more bodies to act upon one another by the force of gravitation. Although this action is known to be governed by the simplest and most exact of natural laws, such interaction of three bodies has hitherto defied man's direct mathematical analysis. Hence we must not hesitate to follow out qualitatively the consequences of a reasonable hypothesis, even if mathematical exactness seems far away.

Let us turn first to the simplest case of definite molecular arrangement in solids, namely, the crystalline forms of the elements. It has been known for a long time that about half of the forty elements which have been crystallographically examined crystallise in the regular system, and that about one-third crystallise in the next most symmetrical crystalline form, the hexagonal. The remaining six elements are less symmetrical. Pope and Barlow point out that in some cases, at least, the departure from isometric symmetry is not great, and probably would suggest explaining the distortion by the deformation of their incompressible "spheres." But will this account for all the cases, and is not the idea that the atoms are compressible better able to explain them all? Assuming that the elementary substances are composed of closely packed equal spheres, these investigators do not seem to have attached quite enough weight to the fact that elements are not always necessarily composed of monatomic molecules. In such a solid, the conditions described by Pope and Barlow would be expected to appear, even if the atoms compressed and distorted one another by their equally distributed affinity; for they would do this equally in all directions, and as far as symmetry was concerned would behave just in the same way as accumulated spheres, although they were actually compressed into tubes, dodecahedrons, or hexagonal forms. Even, however, if such elementary substances as solid mercury or metallic copper possess monatomic molecules, we have very good reason for believing that many other elements do not. To be sure those elements possessing diatomic molecules such as chlorine and bromine could also build up cubical crystals; but this might not be so easy with more complex aggregations. It seems very highly probable that several elements (for example, phosphorus and arsenic) possess at least four atoms to the molecule in the solid state, because we can hardly imagine the solid molecule to be less complex than the vaporised one; and sulphur probably is yet more

complicated. The form which determines the crystal must be the form of the molecule or some multiple of it, and evidently one cannot imagine molecules of four atoms to assume easily forms as simple as those taken by monatomic molecules. The existence of a polyatomic molecule must indicate that in the solid the element combines with itself in two different ways; in the first place very firmly to build up molecules from atoms, and in the next place less firmly to cause these molecules to cohere, forming the solid substance. Obviously if atoms are compressible, they will be more compressed by the powerful forces holding the molecule together than they will be by the less powerful cohesive affinity. Hence must arise irregularly shaped atoms and molecules giving opportunity for varied symmetry in external crystal form.

Thus such elements as copper and silver, possessing probably very simple molecules, would be expected to crystallise in the isometric system, whereas elements such as arsenic and sulphur with more complex molecules would be expected to assume less symmetrical shapes. This is exactly what really happens. Thus it appears that the theory of compressible atoms explains the crystalline form of the cubic and hexagonal elements as well as Barlow and Pope's theory, and also that it reveals much more clearly than that theory the probable cause of less symmetrical crystal forms in the cases of polyatomic molecules.

From the elements we may turn to the binary compounds. Barlow and Pope assume that each element in a binary compound possesses the same atomic volume,—that the formation of caesium chloride, for example, from caesium with an atomic volume of 71, and chlorine with an atomic volume of 25.7, would cause both chlorine and the caesium to occupy the same atomic volume, 21.4 (the molecular volume of caesium chloride being 42.4). They seem to regard the cubic form of such compounds as affording evidence that the two atoms assume the same size when combined; but in reality it is quite as easy to conceive of the formation of a cube from molecules composed of two unequal atoms as from those composed of two equal atoms. A diagram is appended to illustrate this fact. This diagram refutes much of Barlow and Pope's



Diagrammatic sketch showing in perspective how compressible spheres of two very different sizes may build up a cube when pressed together. (This may be supposed to represent the imaginary "crystal unit" of caesium chloride).

reasoning without further discussion. On the other hand, among binary compounds composed of atoms of unequal size, we should expect to find a decided diminution in the occurrence of hexagonal symmetry, because the unequal binary compound would not so well lend itself to this form of symmetry. This is indeed exactly what the facts quoted by Barlow and Pope indicate. Among 67 binary compounds studied, 68.5 per cent (instead of 50

per cent as in the case of the elements) crystallise in the isometric system and only 19.5 per cent (instead of 35 per cent as in the case of the elements) crystallise in the hexagonal system. Hence the assumption of inequality in the sizes of the atoms in binary compounds is consistent with the facts.

To return to a specific case, probably both the caesium and the chlorine contract in the act of combination; but as chlorine is somewhat more compressible than caesium, the former may be supposed to contract somewhat more in proportion to its bulk than the latter. If one were to venture to prophesy, one would be inclined to say that chlorine in caesium chloride may have a molecular volume not over 12, and the caesium perhaps about 30. These figures are given only to show the possible order of magnitude of the two, and do not pretend to be a precise prediction as to their values. If the atoms were compressed into almost cubic forms by their mutual compressions, their edges would then bear to one another the ratio of about 2:3 to 3:1, approximately that indicated in the diagram given above. Cubes formed of such molecules, although strictly isometric, would be expected to exhibit hemihedral tendencies; and this expectation is often fulfilled. The diagram gives an interesting idea of the "crystal unit" as distinguished from the molecule. Such crystal units may be supposed to be the entities necessary to relieve metastable supersaturation.

In this connection it should be pointed out that the theory of compressible atoms explains why exact identity in molecular volume or in facial angle is not necessary for isomorphism; slight differences could be adjusted by the elasticity of the component molecules. On the other hand, one would expect to find a limit to the power of compression or adjustment of an atom or molecule to fit into the place occupied by another. Such a limit seems to have been overstepped, for example, by potassium in relation to sodium, for although the chlorides of both crystallise in the isometric system, these salts are not isomorphous, *i.e.*, they will not crystallise together (Krickmeyer, *Zeit. Phys. Chem.*, 1896, xxi., 82). Sodium chloride crystallises usually in unmodified cubes, whereas potassium chloride, although also isometric, shows much more tendency to develop plagihedral or gyroidal faces. Now the atomic volume of sodium is not far from that of chlorine in the elementary state, and they may be supposed to be about alike in the compound. On the other hand, potassium chloride resembles much more that of caesium; its molecules, although still capable of building cubes, may be supposed to form cubes with the hemihedral structure shown in the diagram, because the potassium probably occupies more space than the chlorine. In short, on the basis of the compressible atom theory, one would expect potassium chloride, although still isometric, to have a decided hemihedral tendency, and sodium chloride to have much less hemihedral tendency, as the facts really show.

These heteromorphous relations of common salt and potassium chloride do not seem to be adequately accounted for by the theory of Barlow and Pope, according to which there seems to be no reason why either should show any gyroidal tendency, or why they should not crystallise together; for would not the theory allow sodium to expand to fill the space occupied by potassium? Such an explanation would be no more arbitrary than that chosen in other cases.

Turning now to more complex compounds, the problem of course becomes enormously increased in difficulty. The best method of procedure is that adopted by Barlow and Pope in comparing the crystalline forms of isomorphous or similarly constituted bodies. Pope and Barlow cite the striking and well-known series measured by Gossner of the orthorhombic chloro- and bromoethanes. The table of data is repeated here, arranged in the order of the molecular volumes of these substances (Barlow and Pope, *Journ. Chem. Soc.*, 1906, lxxxix., 1682).

	M. V.	a : b : c.
C ₂ Br ₆	131.8	0.5639 : 1 : 0.3142
C(BrCl ₂) ₂	120.2	0.5646 : 1 : 0.3192
C ₂ (Br ₂ Cl)Cl ₃	116.7	0.5612 : 1 : 0.3171
C ₂ Cl ₆	113.3	0.5677 : 1 : 0.3160

It will be noted that the introduction of chlorine causes a diminution in the molecular volume, and that this diminution is partly dependent upon the place in which the substitution occurs. It is noteworthy also that the symmetrical introduction of chlorine causes a lengthening in the axis *a* in relation to *b*, and that the unsymmetrical substitution shortens the axis *a*. The axis *c* is least in the pure bromine compound.

These are real differences both as to molecular volume and crystal form. The molecular volume varies more than the crystalline form, probably for the reason already stated, namely, that a change in volume produces only the cube root of its proportional effect when applied in any one axial direction.

With these compounds Barlow and Pope compare the *monoclinic* pentabromoethane, having a molecular volume of 126.5 and axial ratios *a* : *b* : *c*, 0.5650 : 1 : 1.5590 ($\beta = 91.19^\circ$). The introduction of the hydrogen instead of bromine causes not only a very great lengthening in the axis *c* but also a decrease in molecular volume and a decided departure from the orthorhombic symmetry. For the sake of bringing this form into harmony with the other four, the commentators have arbitrarily divided *c* by 5. To the figures thus corrected they have then applied their method of calculating "equivalence parameters." This is a mathematical device, based upon the hypothesis of constant valency-volume, which has the effect of reducing rather widely deviating data to much nearer agreement—partly because the last operation suffered by the function is the extraction of its cube root. Under the circumstances, therefore, it is not surprising that the "equivalence parameters" of these five substances show a closer agreement than the original axial ratios. In another connection it will be shown that this method is capable of bringing such very widely different substances into apparent harmony that one cannot but suspect the method to be somewhat too efficient in its harmonising tendency. The study of the actual measurements of the crystals incline one to believe that the substitution of one hydrogen for a single halogen causes more upheaval in the crystallising tendency than is clearly shown by the table of "equivalence parameters."

According to the theory of compressible atoms, however, the facts all seem to be reasonable and need no preliminary mathematical treatment. There are many reasons for believing that chlorine really occupies less space than bromine. One argument is found in the atomic volumes of the elements. Bromine, although far less volatile than chlorine, has even at the same temperature a perceptibly greater atomic volume. If for comparing these elements we choose corresponding temperatures (*i.e.*, like fractions of their absolute boiling-points, for example, 20° C. for bromine and -65° for chlorine) we find that chlorine has an atomic volume of only 21.8 (Knightsch, *Annalen*, 1890, vol. cclix., p. 100), whereas bromine has an atomic volume of 25.5. Doubtless when these elements combine with others, their atomic volumes change, but under similar conditions we should expect chlorine to occupy less space than bromine, and this is what we find in the case of the five compounds cited in the preceding discussion. It is perhaps more than a coincidence that six times the difference between these two atomic volumes, namely, 22.2, is not very far from the actual shrinkage (18.5) in the molecular volume of the substituted ethane when six atoms of chlorine take the place of six atoms of bromine, although such an idea is entirely incompatible with constant valency-volume. We should expect also to find about such changes in the axial ratios as really exist.

(To be continued).

ON THE DETERMINATION OF TITANIUM AS PHOSPHATE.

By GEORGE S. JAMIESON and RICHARD WRENSHALL.

SEVERAL years ago Eric John Ericson (*Iron Age*, Aug. 27, 1903, p. 4) described a method for the determination of titanium in ferrotitanium and its iron ores. The method was based upon the precipitation of titanium phosphate in acid solution by the addition of ammonium phosphate and boiling, after reducing the iron to the ferrous state by means of ammonium bisulphite or sulphur dioxide. He gave the factor 0.336 for calculating the titanium from the weight of the phosphate, assuming that the latter has the formula $Ti_2P_2O_8$.

On account of the simplicity and rapidity of this method its accuracy and application have been studied in this laboratory. Some modifications of the original method have been found desirable, and its application to the separation of titanic acid from alumina has been worked out. A series of eighteen experiments was made with standard solutions of ferric and titanic sulphates containing enough sulphuric acid to keep the salts in solution, but the quantities of free sulphuric acid present were not determined.

The standard titanium solutions employed in this research were prepared from pure potassium titanium fluoride with the exception of one solution made from a titanium oxalate of excellent quality. The titanium salts were converted into the sulphate by repeated evaporation with sulphuric acid in platinum dishes. The solutions were standardised by precipitating the titanium with ammonia from measured volumes, finally weighing the dioxide, and calculating the strength of the solution in terms of titanium. The values obtained were checked by precipitating the titanium by the sodium thiosulphate method and weighing the dioxide.

In each case 15 cc. of 1:1-hydrochloric acid were added to measured volumes of these solutions, water was added to make the volume 100 cc., sulphur dioxide was passed through for ten minutes, the liquid was heated to boiling, and 20 cc. of a 10 per cent solution of ammonium phosphate were added. The boiling was continued for half-an-hour; the precipitate was allowed to settle for an hour or more; it was then filtered and washed with hot water on a Gooch crucible, in which it was finally ignited for fifteen minutes at the highest temperature of the Bunsen burner and weighed. The method of Ericson was closely followed here except that the Gooch crucible was used instead of paper for filtering, on account of the tendency of the precipitate to run through a paper filter. In order to make satisfactory use of the Gooch crucible, it is necessary to use moderate suction and to avoid allowing all the liquid to pass out of the crucible until thorough washing has been effected, for it is impossible to wash the precipitate after it has become compact and has cracked. Except with very small quantities of titanium, the results obtained were satisfactory. Low results were obtained when less than 0.007 gm. of titanium was present, which appear to be due to the failure of the precipitate to collect in a filterable form. It probably remains in a colloidal condition. The writers have found that with such small quantities of titanium less acid must be used, and, after precipitation and boiling, it is advisable to let the liquid stand for at least six hours, then to warm on the steam-bath and filter. With this treatment the loss appears to be no greater with about 0.002 gm. of titanium than with larger quantities.

When an attempt was made to apply Ericson's method to some ores containing 0.5 to 8 per cent of titanium it was found that no precipitate or only a small one was obtained if the ores had been dissolved by treatment with hydrochloric and sulphuric acid and evaporation with a rather large amount of sulphuric acid instead of being dissolved by a potassium bisulphate fusion. This was evidently due to the presence of the large amount of sul-

phuric acid in addition to the hydrochloric acid used. Therefore, when this convenient method for dissolving titanium ores is employed, it is necessary to neutralise the sulphuric acid, best with ammonia, before proceeding with the determination. Titanium ores or minerals not decomposed by the acid treatment just described, are rendered soluble by fusion with potassium bisulphate in the usual manner.

In the analyses in the table given below, the sulphuric acid present in each solution was neutralised with ammonia before adding the hydrochloric acid; the precipitates were allowed to settle at least six hours, then the solutions were heated on the steam-bath for about twenty minutes before filtering.

No.	Fe taken.	Ti taken.	Ti found.	Error.	Cc. 1:1-HCl used.
1.	0.000	0.0019	0.0018	-0.0001	1
2.	0.000	0.0030	0.0027	-0.0003	3
3.	0.000	0.0030	0.0034	+0.0004	3
4.	0.043	0.0010	0.0010	±0.0000	2
5.	0.086	0.0010	0.0009	-0.0001	3
6.	0.086	0.0030	0.0029	-0.0001	3
7.	0.086	0.0010	0.0009	-0.0001	3
8.	0.086	0.0019	0.0011	-0.0008	6
9.	0.086	0.0010	0.0002	-0.0008	6
10.	0.086	0.0039	0.0032	-0.0007	10
11.	0.043	0.0100	0.0101	+0.0001	5
12.	0.043	0.0154	0.0152	-0.0002	5
13.	0.043	0.0154	0.0151	-0.0003	5
14.	0.100	0.0248	0.0245	-0.0003	15
15.	0.100	0.0248	0.0244	-0.0004	15
16.	0.100	0.0260	0.0256	-0.0004	15
17.	0.110	0.0260	0.0258	-0.0002	15

In these experiments a volume of about 50 cc. was used instead of 100 cc., as in the case of the first series of experiments. It will be observed that in the first ten experiments very small amounts of titanium were taken in order to determine the conditions under which they could be satisfactorily precipitated and filtered. It is evident from these experiments that when 1-3 mgrms. of titanium are present it is necessary to keep the amount of free 1:1-hydrochloric acid down to about 3 cc. in 50 cc. solutions, otherwise low results will be obtained.

Experiments were made to find if titanium phosphate could be precipitated in the presence of tartaric acid, and it was found that this could be done quantitatively, although in a recent article Thornton (*Am. Journ. Sci.*, xxxiv., 214) states that titanium cannot be precipitated by any reagent in the presence of tartaric acid. To the solutions containing measured quantities of titanium and ferric sulphates, about 2 grms. of tartaric acid were added, and enough ammonia to make them slightly alkaline. Then hydrogen sulphide was passed into the warm solutions until the iron was reduced and precipitated as sulphide. The solutions were treated with 10-15 cc. of 1:1-hydrochloric acid, depending upon the amount of iron present, and heated until the iron sulphide was dissolved. Then 20 cc. of the 10 per cent ammonium phosphate reagent were added, and the experiments from this point were identical with those described above. In the first four experiments the ferrous sulphide was filtered off and washed with hot water containing a little ammonium sulphide, while in the last four the ferrous sulphide was not filtered, but dissolved as previously directed. No advantage was gained by removing the iron from the solution. The following results were obtained:—

No.	Fe taken.	Ti taken.	Ti found.	Error.
1.	0.086	0.0207	0.0206	-0.0001
2.	0.043	0.0050	0.0049	-0.0001
3.	0.043	0.0030	0.0024	-0.0006
4.	0.043	0.0040	0.0039	-0.0001
5.	0.043	0.0060	0.0059	-0.0001
6.	0.200	0.0249	0.0253	+0.0004
7.	0.100	0.0186	0.0186	±0.0000
8.	0.100	0.0249	0.0248	-0.0001

The choice of methods for the reduction of the iron is largely a matter of personal preference, since both give equally good results as seen in the tables of test analyses given above. However, it may be said that the reduction of the iron in our ammoniacal solution is somewhat quicker than that by sulphur dioxide in a hydrochloric acid solution.

In applying this method to the determination of titanium in some ores, which were previously found to be completely decomposed by acid treatment, the procedure was as follows:—To 0.5 grm. of very finely pulverised sample, 25 cc. of concentrated hydrochloric acid were added, and the solution was heated upon the steam-bath until no further action was observed. About 20 cc. of 1:1-sulphuric acid were added, and the solution was cautiously evaporated to sulphuric acid fumes and then heated for an hour at a temperature just below the boiling-point. After cooling, 30 cc. of water were added, and the solution was warmed until the soluble salts had dissolved. The insoluble matter was filtered, washed three times with very dilute sulphuric acid, and finally with water at room temperature. The insoluble matter was tested, and was found to be free from titanium. The filtrate was diluted to exactly 500 cc., mixed thoroughly, and aliquot parts were taken so that the ignited precipitate would not weigh over 90 mgrms., as it was not practical to attempt the filtration of larger amounts of this gelatinous precipitate. To each aliquot part 2 grms. of tartaric acid were added, and the method from this point was identical with that described above. Three titaniferous iron ores were analysed with the following results:—

Ore.	Ti found (per cent).	Ti by the volumetric method (a) (per cent).
A	13.00	13.18
A	13.17	—
A	13.20	—
B	24.19	—
B	23.99	24.22
B	24.22	—
C	15.82	—
C	15.86	15.94
C	16.01	—

(a) A modification of the method in Gooch's "Methods in Chemical Analysis," p. 242.

It is recommended that for the general application of this method to the determination of titanium in the presence of relatively large amounts of iron, the titanium be precipitated from a solution of about 100 cc. volume which contains 15 cc. of 1:1-hydrochloric acid. Furthermore, it is recommended that enough substance be taken so that at least 10 mgrms. of titanium shall be present in the solution.

It was found that titanium could be separated from aluminium and determined in the same manner as when

iron is present, but that it was necessary to use more hydrochloric acid in order to prevent the precipitation of aluminium phosphate. The method employed was to add 1–2 grms. of tartaric acid to the solution of titanium and aluminium sulphates, and enough ammonia to make it slightly alkaline. (The tartaric acid was used to prevent the formation of the hydroxide). Then a measured quantity of hydrochloric acid was added and the analysis was completed in the same way as when iron was present. A volume of about 100 cc. was used in the accompanying experiments. (See Table preceding column).

These experiments indicate that with a volume of 100 cc. containing 0.05–0.15 grm. alumina it is necessary to have an excess of at least 8 cc. of concentrated hydrochloric acid in order to get a satisfactory separation of the titanium.—*Journal of Industrial and Engineering Chemistry*, vi., No. 3.

PROCEEDINGS OF SOCIETIES.

SOCIETY OF CHEMICAL INDUSTRY.

THE Thirty-Third Annual General Meeting of the Society was held in the large Lecture Theatre of University College, Nottingham, on Wednesday, July 15, 1914, the President, Dr. RUDOLPH MESSEL, F.R.S., in the chair.

The Mayor of Nottingham, Mr. FREDERICK BALL, attended to offer a welcome to the members on behalf of the City. He said that as the representative of a city whose past was crowded with historic events of national importance, and whose Castle has been the home of Kings and Parliaments; as the representative of a city, the interest of which was bound up with the industrial and commercial development of our country, he had the privilege and honour to give them a cordial welcome, and to hope that their deliberations might be profitable to industry and manufactures. Many people had formed an opinion that this country had not made the advance in chemical science and manufacture attained by others. If there were any truth in such an opinion he trusted that this Society would see to it that this stigma was removed, and that British manufacturers would have as much aid from chemical science as their competitors abroad. King George, when Prince of Wales, on his return from his Empire tour, and speaking at the Guildhall on December 5, 1901, had said "Wake up England!" He was sure the Society was alive to the important part it could play in giving effect to that injunction. The aid chemical science could render to the local trades of bleaching, dyeing, and dressing of lace and hosiery fabric, was beyond conception. The municipality of Nottingham was alive to the importance of imparting knowledge of chemical science as applied to industry and had, through the University College, given every facility for its study, especially in connection with the staple trades.

THE PRESIDENT, in acknowledging the welcome, desired on behalf of the Society of Chemical Industry to offer their cordial thanks for the hearty reception which the Mayor had given to them. The Mayor was perfectly right to remind them of the words of the present King, when, as Prince of Wales in 1901, he said "Wake up, England!"; he was also right to expect that the Society should do great things for chemistry and industry. As far as chemical industry was concerned, His Majesty's words held as good to-day as they did in 1901. It was true that they had made considerable strides in many directions, especially in this district; still they had a great deal of leeway to make up. It was curious that many inventions which had their origin here in England seemed, after all, not to have been worked in this country as they ought to have been. British manufacturers ought to take up new industries. As a case in point, he referred to the synthetic production

No.	AlO taken.	Ti taken.	Ti found.	Error.	Cc. conc. HCl used.
1.	0.063	0.0273	0.0277	+0.0004	10
2.	0.060	0.0310	0.0308	-0.0002	12
3.	0.070	0.0248	0.0245	-0.0003	10
4.	0.063	0.0248	0.0249	+0.0001	9
5.	0.110	0.0210	0.0214	+0.0004	10
6.	0.100	0.0260	0.0263	+0.0003	11
7.	0.120	0.0310	0.0309	-0.0001	14
8.	0.060	0.0223	0.0224	+0.0001	15
9.	0.060	0.0186	0.0189	+0.0003	8
10.	0.050	0.0186	0.0182	-0.0004	15
11.	0.070	0.0248	0.0245	-0.0003	10
12.	0.060	0.0122	0.0119	-0.0003	7
13.	0.050	0.0248	0.0292	+0.0044	5
14.	0.100	0.0310	0.0473	+0.0163	5
15.	0.150	0.0186	0.0233	+0.0047	7
16.	0.100	0.0248	0.0288	+0.0040	5
17.	0.070	0.0310	0.0351	+0.0041	7

of ammonia, the invention of Prof. Haber; he did not see why this could not be made one of the great industries of this country, where the facilities for carrying it on were equal to those in Germany. He regretted, however, to say that there was no indication of any intention to take it up in this country. It was not only a case of "Wake up, England," but of "Wake up, masters," to whom he would say: "Be less conservative, and see that you take advantage of everything that science offers and that energy can accomplish."

The President said the meeting in Nottingham had promised to be one of the most illustrious ever held by the Society. They had expected Sir William Crookes and Sir Henry Roscoe to be present. Both were octogenarians, Sir William Crookes being 82, and Sir Henry Roscoe in his 82nd year. At the last moment neither of those gentlemen was able to come on account of ill-health. They knew, of course, that Sir William Crookes was his predecessor in office, being elected last autumn, but he had very soon to retire because a great honour was done to him and through him to their Society, by his being elected President of the Royal Society—the greatest scientific honour in this country, and it was an unwritten law of the Royal Society that its President should hold no similar office simultaneously. The Royal Society had only had two chemical Presidents in a century, the first one being Sir Humphry Davy and the second their worthy President, Sir William Crookes.

ADDRESS OF SIR WILLIAM CROOKES, O.M., Pres. R.S.

In the absence of Sir William Crookes his Address was read by the President, as follows:—

I fear that you may feel a little ennuied at being called upon to listen to a Presidential Address delivered by one who no longer has the honour of being your President. But I cannot forego the opportunity of expressing my regret at being compelled to resign my position. My election to the Presidency of the Royal Society makes it impossible for me to continue to hold the office, but my interest in the Society of Chemical Industry, of which the Nottingham section is so vigorous and flourishing a branch, can suffer no diminution. My regret at parting is greatly tempered by the reflection that in Dr. Messel, who has consented to step into the gap, the Society will have a President of preeminent suitability and unrivalled qualifications. There is little need for me to remind you that Dr. Messel's knowledge of Industrial Chemistry and his close connection and acquaintance with foreign manufacturing practice will be of great value to English Chemists. His work on the industrial applications of Catalytic processes has brought him world-wide fame, and our Society is fortunate in having a man of such eminence at the head of its affairs. I must congratulate you heartily upon the energy and enterprise displayed by your Members, and upon the success of the work accomplished. Technical chemistry makes great strides. The past year has seen the publication of results which, although perhaps not sensational enough to stir public imagination, nor intrinsically important enough to be described as epoch-making, are a sufficient tribute to the steady industry of investigators, to their resource in overcoming difficulties, and their acumen in elucidating the causal relations of some particularly interesting phenomena.

Foremost I must mention Haber's process for the production of Ammonia. Ammonium sulphate is now synthesised by the Badische Company, which is about to enlarge their plant by the end of 1915 to a capacity of 130,000 tons per annum. The catalyst osmium has been replaced first by uranium, later on by Fe_2O_3 . The investigation of the process has shown that the latter catalyst is made more active by the addition of certain substances, e.g., oxides, hydroxides, and salts of alkali metals, while other substances, such as arsenic, act as specific poisons towards ammonia catalysts.

The demand for nitrogenous fertilisers steadily advances. There is also an increasing demand for nitrogenous pro-

ducts for industrial purposes, concentrated nitric acid being one of the most important of these products. The Norwegian Hydroelectric Nitrogen Company, Limited, among others, have worked out a simple method of obtaining dilute nitric acid by the oxidation of atmospheric nitrogen, and then concentrating the dilute acid by making use of the hot gases of the furnaces. The concentrated acid can thus be very cheaply obtained. The Norwegian Company find that the pure acid can be transported in aluminium tanks. A steamer equipped with aluminium tanks for 40 tons is already in regular service between Notodden and Engene on the Christianiafjord, and designs are in progress for 600 to 700 tons tank steamers for regular service to England and the Continent. The output of the Company's work at Rjukan and Notodden have now reached—

80,000 to 90,000 tons of nitrate of lime,
10,000 tons of nitrite of soda,
5,000 to 6,000 tons of refined nitrate of soda,
15,000 tons of nitrate of ammonia.

The work of Dr. E. J. Russell and others on the action of antiseptics on soil in increasing the growth of crops has led to deeply important results. The anomalous effects of the partial sterilisation of the soil in causing first a fall and then a rapid rise in the number of bacteria, were first observed. Further study showed that the increased productiveness of partially sterilised soil is due to the increased production of ammonia, and that the increase in bacteria is the result of an improvement of the soil as a medium for bacterial growth. From the experiments Dr. Russell concludes that ordinary soil contains a factor which limits the bacterial population and prevents its reaching its maximum. The search for this soil organism revealed the presence of many protozoa, now being examined from a zoological point of view. The fact that the detrimental organisms are more easily killed than the useful organisms explains many paradoxical results—such as the ultimately beneficial influence on productiveness of long-continued frosts and droughts, which are harmful to organisms. The "sickness" of greenhouse soil has been investigated; it is found that it may be ascribed to two causes—an accumulation of pests and an abnormal development of factors detrimental to bacteria. Methods are now in progress for the partial sterilisation of the soil on a large scale. The action of different antiseptics has been studied and interesting conclusions drawn from the work. It is found that there is a decided difference in the action of different antiseptics; only actual trial will decide which may be best in special cases. Generally speaking formaldehyde and pyridine are the most useful for sick soils; cresol, phenyl, &c., coming next, while the higher homologues of benzene are the least effective. None of these, however, answers as well as steam—the most efficient of all sterilisers.

A remarkable achievement in technology is due to a member of our Society who recently died. I refer to H. Frasch—to whom the Society's Perkin Medal was awarded in 1912. Frasch successfully solved the problem of the extraction of sulphur from the deeply buried deposits of Louisiana. He conceived the idea of melting the deposit *in situ* by means of superheated steam, and forcing the molten sulphur to the earth's surface through an inner tube. The process has worked satisfactorily and large quantities of sulphur are thus extracted.

An interesting modern process is that of Dr. Walther Feld, whose death in his prime is a severe blow to Science. A strenuous worker of great originality Feld has enriched technology with many discoveries; the most important relates to the preparation of ammonium sulphate direct from crude coal-gas. The problem of the utilisation of the sulphur of the crude gas has thus been completely solved by a particularly neat and ingenious method. Using ammonium polythionate, ultimately obtaining ammonium sulphate, sulphur, and sulphurous acid, the two latter are again utilised in the process, while the ammonium sulphate

is obtained by evaporating the solution. The practical value of a process in which ammonium sulphate is obtained without the use of sulphuric acid is obvious. The researches of Feld in working out the details of this method also throw light upon many interesting scientific questions.

Another method of fixing nitrogen by utilising the sulphur of coal is that of K. Burkheiser. In this process bog iron ore is used to absorb the sulphuretted hydrogen, and the sulphurous acid produced from it is used for the formation of a mixture of ammonium sulphate and sulphite. The process is working at Flemalle Grande, near Liège, in Belgium, and is giving satisfactory results.

Recent work on the synthesis of Rubber has attracted much attention, and notable advances have been made. As long ago as 1882 Tilden noticed that isoprene is converted into rubber by certain chemical reagents; ten years later he showed that the synthetic product obtained from isoprene is capable of vulcanisation. Subsequent work led to the recognition of the fact that most substances containing a conjugated double linking tend to polymerise, the polymers ranging from sticky substances through well-defined rubbers to hard resins. Polymerisation may be spontaneous, or it may be brought about by chemical reagents—acids or alkalis—by heat, or sunlight. In 1908 it was simultaneously discovered by C. Harries and F. E. Matthews that sodium is an excellent agent for the polymerisation of isoprene. The action is practically quantitative, and is not affected by the presence of impurities. Moreover, it takes place in the cold, or on heating very moderately. Harries showed that a superior quality rubber could be obtained by the polymerisation of butadiene. Research showed that the isoamyl alcohol obtained from commercial fusel oil was the most suitable material to work upon. By means of dry hydrochloric acid it was converted into the chloride, and then chlorinated to give the dichloride, from which the hydrochloric acid was eliminated by passing over hot soda-lime. The isoprene was then sealed up with 3 per cent thin sodium wire, and heated for several days to 60°. The dark brown product thus obtained was treated with acetone to precipitate the rubber.

To get cheap fusel oil Fernbach has worked out a new process of fermentation, starting with starch. Holt has recently made some valuable discoveries relating to the manufacture of isoprene from the fraction of petroleum of lowest boiling-point, and the preparation of butadiene from benzene or phenol, tetrahydrobenzene being formed as intermediate product. He has also observed that isoprene when treated with sodium in an atmosphere of carbon dioxide gives quite different products from those obtained by the same action in air. No perceptible change occurs at first, but finally a black voluminous mass is obtained, which gives pure white caoutchouc with water or alcohol. Recent work shows that all synthetic caoutchoucs differ chemically from natural caoutchouc. Physically the vulcanised products from synthetic (isoprene) caoutchouc are equal in quality only to products from medium grade natural rubbers.

Another series of remarkable syntheses is due to Fischer and Freudenberg, who, starting from gallic acid, have succeeded in obtaining lichen constituents and tannins, for which the general name "depside" has been suggested.

The process recently patented by Dr. F. Bergius for the preparation of hydrogen, and his investigations of the preparation of coal from cellulose at high temperatures and pressures are of deep interest. At high temperatures water acts as a fairly strong acid or base, provided it is kept liquid. In presence of a metal such as iron hydrogen is evolved. The gas is obtained in a pure state and the speed of the reaction is very high. The cost of production is about $\frac{1}{2}$ d. per cubic metre at atmospheric pressure, and this would be reduced in large plants; it is considerably less than that of the cheapest method now known.

Water kept liquid by high pressures acts as an excellent thermostat in consequence of its high specific heat; this fact can be applied in the preparation of coal by the decom-

position of cellulose. The product has all the chemical properties of natural coal, though physically it differs from it. If, however, the temperature and pressure during formation are greatly increased a substance is obtained which closely resembles anthracite. The specific gravity increases with the duration of compression and the temperature employed.

The use of hydrogen in the hardening of fats has recently found favour. The natural supply of hard fats is absorbed in the manufacture of margarine and other foodstuffs—hence for soap-making and other similar purposes artificially hardened fats are employed. Whale oil gives a good fat for soap-making when hardened in presence of reduced nickel; the product seems likely to be useful for lubricating and other purposes.

I may perhaps be allowed to allude to such parts of my own work as may be of interest to Industrial Chemists. Such are the investigation of the spectrum of silicon in a very pure state, and also the preparation of eye-preserving glass for spectacles. The main object of this last research is to prepare a glass which would cut off those heat rays from molten glass which are injurious to the eyes of workmen, without obscuring too much light, or materially affecting the colours of objects seen through the glasses. The research was afterwards extended to the examination of the screening properties of different glasses for ultra-violet and luminous rays, and many specimens of glasses containing known quantities of pure metallic oxides and earths were prepared in my own laboratory. I succeeded in obtaining a glass which cut off 98 per cent of the heat rays, while others, which I have called "Anti-glare Glasses," cut off practically all the ultra-violet and a considerable proportion of the heat rays. I am now investigating the question of the choice of a glass which will reduce to a minimum the fading and alteration of the colours in water-colour paintings on exposure to sunlight and diffused daylight. This series of experiments is not yet concluded.

In spite of the advances which I have just briefly brought to your notice, and notwithstanding the fact that the active investigation of scientific and industrial problems is going on at a rapid rate, the World is greatly in need of able Researchers, perhaps more so now than at any previous time in its history. We may be certain that discoveries of vast importance are waiting their Newtons. Secrets of nature are lying hidden ready to disclose themselves to the "immortal mind." But is not the attitude of the public towards investigators lacking in understanding and imagination, and do not the authorities treat Scientific exploration in a niggardly spirit? Scientific men have to deplore the fact that there appears to be a lack of men gifted with the genius for Research and for grappling with the Riddles of the Earth. Scientific research has been and is being starved. It is high time measures should be taken to remedy this state of affairs, which otherwise can only end disastrously for the nation. I do not wish to come before you as an alarmist, but rather as one who can diagnose the disease and suggest the remedy. I know you will be in hearty and enthusiastic agreement with me when I say that the allotment of public monies to the furtherance of scientific work, the tangible recognition of the services of scientific men, the provision of opportunities for all kinds of investigations of scientific problems without reference to their immediate commercial value—these are the benefits we look for at the hands of Government and of the Nation. And what are our responsibilities and duties in regard to research? I think our chief care should be to see that we encourage and cultivate the right type of man for research work. We should make more definite efforts to select suitable men from among our students and to train them to the highest point of efficiency, after having made up our minds what are the special qualities we need. I think we can learn a great deal from the training of our Army Scouts. Our researchers are actually Scouts, penetrating strange and unknown countries, and the keys to success are the same as for all scouts. The principal qualifications are confidence,

keenness, intrepidity, inspiration. The knowledge that you are well equipped for your work, the belief that your training has been thorough, and that you have made the best possible use of it, should develop in you the self-reliance and boldness indispensable in a scientific scout; other valuable qualities, quickness of eye and mind, and the power of reasoning and expression, can undoubtedly be developed and perfected. And what can be promised as the reward of scientific work?—"Not the reward, the work makes man sublime." Perhaps after all only the Fight, the Struggle, the Search but Research, like Virtue—

"Desires no isles of the blest, no quiet seats of the just,
To rest in a golden grove, or to bask in a summer sky:
Give her the wages of going on, and not to die."

Dr. MESSEL, having read the address said—You will agree that it is very remarkable that a man, the greater part of whose life work has been devoted to scientific research, should take an interest in technology such as is shown in his address, which I have just had the pleasure of reading to you. He does not, however, do himself justice. He refers here to the famous Haber process for the synthetic production of ammonia, and to the Norwegian process for the production of nitric acid and nitrates in various forms, but not a word does he say as to whom all this work is in the first instance due. It is, I contend, due to no one else than our Past-President, now the President of the Royal Society, Sir William Crookes. He says at the end of his address here: "I do not wish to be an alarmist." In his address on the great food problem before the British Association in 1898 he undoubtedly seemed to be an alarmist lest our food supply could not keep pace with our requirements. He pointed out that ever larger quantity of manurial material would be required if food supplies for future generations were to be sufficient to meet the enormous increase of population and its requirements. But though it may be right that he was an alarmist, yet he has rendered a great service by calling attention to the facts. Not sufficient stress, however, is laid on the fact that, as a true physician, he likewise prescribed the remedy. In his address of 1898 he asked if it was not possible to solve this momentous problem, and he proceeded to describe the fixation of nitrogen as vital to the progress of civilised humanity. Not only in general terms did he refer to it, but he pointed out that as far back as 1892 he had exhibited before the Royal Society an experiment on "The Flames of Burning Nitrogen." This method has since been made use of by Lord Rayleigh for the purpose of eliminating nitrogen from the air, with the object of producing argon. The data thus obtained Crookes made use of in calculating the cost of nitrate of soda, and he proceeded to show that electricity produced by means of coal and steam engines would be too costly for industrial purposes, but that at Niagara, where water power was utilised, electricity was sold at one-seventeenth of a penny per Board of Trade unit, and at this rate nitrate of soda would not cost more than £5 per ton; the limit of cost, however, has not yet been reached. He also pointed out that Niagara alone was capable of producing all the energy required without materially reducing its mighty flow. The address in question has thus called attention to the necessity of producing and fixing nitrogen in some way or another for the purpose of increasing crops. Sir William likewise shows how absolutely practicable it would be to combine atmospheric nitrogen, which costs nothing and which is at our hands in such quantities that it can never be a question of our having to starve, if only we make use of it. True there have come after him other inventors, one greater perhaps than the other, devoting themselves to nitric acid and ammonia problems, and I do not for one moment wish to take away the credit from these great men who have built up these great and new industries. On the contrary. But I am equally anxious to give credit where credit is due, and to point out that these vast problems were really first of all suggested here in our country, and that the

impulse to achieve these great results was primarily due to the foresight of an Englishman, Sir William Crookes. Then, again, his reference to the work he has done with regard to the discovery of a glass that enables people to work at furnaces without suffering injury to eyesight, is of the greatest importance. He also refers here to a paper on the production of hydrogen for use in connection with the hardening of fats and the production of ammonia. But one of Crookes's very early investigations and discoveries was that of thallium in 1862, and it is noteworthy now, after more than fifty years, that this work has found practical application in a recently patented process involving the use of thallium chloride in producing hydrogen. I could not refrain from making some comments on the work and address of Sir William Crookes, and I ask you now to accord a hearty vote of thanks to him.

Prof. G. G. HENDERSON seconding, referred to the fact that Dr. Messel had omitted to read Sir William Crookes's reference in the early part of his address to himself. Having read the passage in question, Prof. Henderson reminded them that three years ago, in recognition of his scientific achievement and of his services to the Society, Dr. Messel was elected to the Presidential chair, that he had discharged the duties of his office for the normal period with the greatest advantage to the Society, and that also during the following year, when the chair was occupied by Prof. Bogert, Dr. Messel was acting as president during Prof. Bogert's absence from this country; and finally, when the Royal Society had risen up in its might and taken away from them their President, the Council had unanimously agreed to ask Dr. Messel to fill the gap thus created, believing that in the interests of the Society, though unusual, he would consent so to act. This was a unique record. The Society was under a debt to Dr. Messel, which it would be very difficult to pay, but at least they recognised their indebtedness by offering him their most cordial thanks. That he would ask them to do.

The resolution having been supported by Mr. EUSTACE CAREY, was carried unanimously.

The PRESIDENT, in acknowledging the vote, said that the members having again shown their confidence in him, and having received him with such heartiness, he could only say how very greatly he appreciated their kindness towards him. The fact that he had the heartiest support of everybody made it possible for him to have a successful year of office once more. If he had done anything for the Society in the past he was only too delighted to have done it, and he was equally ready to assist the Society in the future.

Presentation of the Society's Medal.

The PRESIDENT then proceeded to make the presentation of the Society's medal, the recipient being the Right Hon. Sir Henry E. Roscoe, LL.D., F.R.S., who was unable through indisposition to be present. Dr. Messel first read a telegram from Sir Henry, sending affectionate greeting and wishing success to the meeting, and also a letter expressing his sincere regret that he found it impossible to attend to receive at the President's hands the medal with which the Society had honoured him. He felt confident that his enforced absence would not be taken by the members as indicating either want of interest on his part in the proceedings of the Society or of gratitude to them for the award of the medal. With regard to the first point, that was impossible for a man who was present at the birth of the Society, acted as its first President thirty-three years ago, and since then had watched its progress from year to year and rejoiced in its increasing usefulness. As regarded the second point, all he could say was that the honour was a great one, and for any service he had rendered to the Society in the past he had been more than amply repaid. Sir Henry then referred to the origin of the Society and mentioned that one of its objects was to promote a good understanding and friendly intercourse between professional and industrial chemists.

The recipients of the Society's medal form a record of

eminence in pure and applied chemistry and in the furtherance of the objects of the Society, of which any association may feel justly proud. The addition of the name of the Right Hon. Sir Henry Roscoe, which has already been announced by the Council of the Society, will add further lustre to our roll of medallists, and will, I feel sure, be welcomed most heartily by every member of the Society.

According to our Charter the recipient of the medal shall be a person who, in the opinion of the Council, has rendered conspicuous service to applied chemistry, or to the Society in furtherance of its objects.

Sir Henry Roscoe's long record of eminent service both to chemistry and to the Society needs no words of mine to justify our selection, but I may be permitted to recall something of the work of his distinguished career, especially at a time when modern advances in science are apt to make us unduly forgetful of the past.

Roscoe's earliest researches, which were conducted in conjunction with Bunsen nearly sixty years ago, were on the measurement of the chemical action of light, a series of investigations which laid the basis of quantitative photo-chemistry and which have played a large part in modern developments of the photographic industry. Some few years later, during the early days of his tenure of the Chair of Chemistry at Owens College, Manchester, he carried out his well-known work on the composition of the halogen acids of constant boiling-point and on perchloric acid. Then followed in 1868 his classical research on vanadium. Roscoe proved that the substance previously described as vanadium by Berzelius was, according to the method adopted in its preparation, either an oxide or nitride. He was the first to isolate the element and to assign to it its right place in the periodic classification; in addition he determined its atomic weight and prepared a large number of new vanadium compounds.

It is worthy to note that with all the improvements suggested by the vast amount of research work on atomic weights, both in America and in this country, practically no difference is found in the latest determinations of the atomic weight of vanadium. Many valuable technical uses of vanadium have followed in the wake of Roscoe's discoveries. Vanadic acid has been employed as an oxidising agent in the aniline colour industry, whilst it has received many important applications in metallurgy.

Apart from these direct services of Roscoe's own work to applied chemistry, he has contributed a large indirect share to the advance of chemical technology through the conspicuous success of the School of Chemistry he established at the Owens College (now the University), Manchester. During the thirty years of his professorship—from 1857 to 1887—close on 2000 students passed through the curriculum of his laboratories. Of these many occupy positions of trust and responsibility in chemical industry and have contributed much to the advancement of applied chemistry.

Roscoe's association with this Society commenced with its inception and his selection as its first President was an augury of its future success which has been so amply realised. He gave his active support to making the Society a national institution and secured the interest of many notable chemists in its work. Throughout the life of the Society Sir Henry's interest in its welfare has never waned, and we owe much of its progress to his stimulating activity.

I must not omit one other feature of Roscoe's many-sided labours which has reflected on our welfare, his work in technical education. With a firm belief in the efficacy of scientific training, he taught his students and his fellow citizens in Manchester to realise the value of the application of science to industry. He was a member of the first Royal Commission on Technical Education, and during his subsequent Parliamentary career took every opportunity to forward the means for the technical training of chemists and to bring the best methods for the education of future captains of industry before the authorities concerned.

The success that has marked all Roscoe's work in its exceptional breadth and thoroughness is the most lasting memento of its merit. Its recognition by the members of this Society is but one further record of appreciation to the many that have been accorded to him. It is the highest honour we can confer on one who has done much for the advancement of chemical industry and who by his wonderful personality and high character has endeared himself to us all.

May he long be spared to us!

Dr. Messel intimated that Sir Henry had asked him to receive the medal on his behalf, and he would hand it to him in due course in the name of the Society.

Next Year's Meeting.

Mr. J. HÜBNER said the Council had kindly accepted an invitation to hold the next Annual Meeting of the Society in Manchester, and it was his pleasant duty to extend to the Society a most hearty welcome. In 1915 they would be in an exceptionally fortunate position as the British Association were to meet in Manchester and extensive preparations for it would be made. Many of these he had no doubt their Society would also be able to enjoy.

Mr. HOSEASON supported the invitation, which was unanimously approved, and the President, on behalf of the Society, tendered to Manchester a hearty vote of thanks for the invitation.

Thanks to University College.

The PRESIDENT said that they were grateful to the authorities of University College for lending them that splendid room. The interests of the Society were identical with those of Colleges like the one in which they met. Colleges had the greatest interest in keeping in touch with applied science, which was very often their future bread and butter; and the Society had also the greatest interest in keeping in touch with the colleges so as to know what was going on in them and keeping these things before them.

Sir JOHN TURNER said he had been asked to second the vote, but it seemed rather strange that he should be doing so, because indirectly he was associated with that institution as a member of the City Council, which he had been for a few years. However, he would like to say on behalf of the people who controlled the work in this College that they were always willing to do all they possibly could to forward that which was for the benefit of the people in regard to things scientific or practical.

The meeting then closed.

NOTICES OF BOOKS.

The Fixation of Atmospheric Nitrogen. By JOSEPH KNOX, D.Sc. London: Gurney and Jackson. 1914.

THE aim of this monograph is to give a succinct account of methods of fixing atmospheric nitrogen which are actually employed technically, laying special stress upon the theory of the processes. The preparation of nitrous and nitric acids and their salts is treated first and most fully. Theoretical considerations are discussed at some length, and copious references are given to the literature of the subject, while short descriptions are included of the processes which are at present being worked successfully on a large scale. The synthesis of ammonia and ammonium compounds is next described, the work of Haber and his collaborators being fully treated. Finally, some account is given of the conversion of atmospheric nitrogen into compounds such as nitrides, cyanides, &c., which readily yield ammonia.

Report of the Agricultural Research Association, 1913.

THE Agricultural Research Association, which has had nearly forty years of useful life, has for its object the investigation of agricultural problems and the extension of knowledge of agricultural science. The Director's report contains some account of the three-year trials carried out at the Station of the action - hurtful or otherwise—of living things upon plants. Recent work on the action of antiseptics on soils is criticised very freely, and when the Director shows great asperity about the incredulity of the public as to certain of his results he possibly overlooks the fact that he himself very summarily rejects the work of some other investigators. The report gives some brief account of the past work of the Association, and in particular the claim is put forward that it has been definitely established that all green plants absorb nitrogen from the air, and that there is not a particle of evidence for the belief in the existence of nitrifying bacteria in the soil.

Lectures on Explosives. By WILLIAM MACNAB. London: The Institute of Chemistry of Great Britain and Ireland. 1914.

THIS book contains two lectures delivered before the Institute of Chemistry, and intended to give advanced students an insight into the work of professional chemists. In the first lecture the nature of explosive phenomena and the general properties of explosives were discussed, and methods of testing them were explained in some detail. The second lecture gave an account of the manufacture of explosives, special attention being paid to the restrictions imposed by the Home Office. The lectures will be found very stimulating and interesting by young students, although the lecturer was unable to do more than give an outline of the subject, and the text of them will be very acceptable to those who were not so fortunate as to be able to be present at them.

CORRESPONDENCE.

"PHOSPHORESCENCE" OF SULPHUR.

To the Editor of the Chemical News.

SIR,—I hope that Dr. Léon Bloch will accept my assurance that the omission from my article on the "Glow of Sulphur" of any reference to his researches was quite unintentional. I thought I had made a careful search through chemical literature for accounts of previous work on the subject, but for some inexplicable reason I did not discover Dr. Bloch's papers. Had I done so, I might have been spared much subsequent labour, but at any rate it may be some satisfaction to him to have an independent confirmation of some of his results.

On one point only am I unable to agree with Dr. Bloch's conclusions. He attributes the "phosphorescence" to oxidation of sulphur vapour, but my own experiments all seem to show that it is due to the oxidation of minute particles of solid, or more probably liquid, sulphur.

Apologising for the injustice I have unwittingly done to Dr. Bloch, and thanking him for the correction.—I am, &c.,

W. H. WATSON.

MELTING-POINT OF CANE-SUGAR.

To the Editor of the Chemical News.

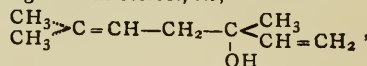
SIR,—I notice that "Van Nostrand's Chemical Annual" (1909) gives the melting-point of cane-sugar ($C_{12}H_{22}O_{11}$) as 189.2° (corrected), a figure somewhat higher than that found by your correspondent as given in the current issue of the CHEMICAL NEWS.—I am, &c.,

F. H. LORING.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 22, June 2, 1914.

Constitution of Linalol.—Ph. Barbier and R. Locquin. —Barbier has suggested that linalol is a primary alcohol of formula $\begin{matrix} CH_3 \\ | \\ CH_3 > C = CH - CH_2 - CH_2 - C \begin{matrix} \nearrow CH_3 \\ \searrow CHCH_2OH \end{matrix} \end{matrix}$, while Tiemann and Semmler regard it as a tertiary alcohol. It may be shown that 2.6-dimethyloctanol-6 and tetrahydro-*l*-linalol are identical, and that the OH groups in the two compounds have the same nature and occupy the same position. Hence Tiemann and Semmler's formula must be regarded as correct, *i.e.*—



and Barbier's formula must be abandoned. Apparently in the formation of geranyl acetate from natural *l*-linalol under the action of acetic anhydride and in similar reactions a curious molecular transposition takes place, a tertiary alcoholic function changing to a primary alcoholic and finally to an aldehyde function.

Researches on Acyclic γ -Halogen Acids.—Henr Wohlgemuth.—The author has investigated the action of hydrazids on γ -valerolactone, thus getting three *n*-valeric- γ -halogen acids, which he has submitted to treatment with various reagents. The three acids are readily etherified, giving stable ethers. The γ -halogen ethers do not react with magnesium, and in general it may be said that the halogen is much less active in halogen ethers when it is in the γ - than in the α - and β -positions. This relative passivity may be attributed to a "steric hindrance" resulting from the proximity in space of the ether salt and halogen derivative functions in the 1.4-positions.

Migration of a Methoxy Group in the Decomposition of a Quaternary Ammonium Hydrate by Hoffmann's Method.—M. Tiffeneau.—When the derivative obtained by the action of amines upon the methylodohydrine of asymmetric methylphenyl glycol is decomposed, water and trimethylamine are eliminated, and the methoxy group migrates, the final product being $C_6H_5-CH_3=CHOCH_3$. There is thus no modification in the carbon skeleton, which remains branched like the original compound.

MISCELLANEOUS.

Institute of Chemistry.—Pass List, June—July (1914) Examinations.—Of twenty-three candidates who presented themselves for the Intermediate Examination eleven passed—A. J. Boyd; R. G. Browning; R. C. Dennington; A. O. Jones; J. King; E. Leitch, B.Sc. (Glas.); G. W. Moore; P. D. Oakley; P. W. Rait; E. L. J. Stockdale, B.Sc. (Lond.); and H. M. Webb. Of twenty-eight candidates who presented themselves for the Final (A.I.C.) Examination, thirteen passed:—In the Branch of Mineral Chemistry—H. Trickett and H. Vernon, B.Sc. (Lond.). In the Branch of Organic Chemistry—J. G. Duncan; T. H. Durrans, B.Sc. (Lond.); S. H. Groenewoud; L. A. Jordan, B.Sc., A.R.C.S. (Lond.); L. Orange, B.Sc. (Lond.); W. S. Ritchie, B.Sc. (Lond.); F. W. Snelgrove, B.Sc. (Lond.); J. W. Tait, M.A. (Edin.); and F. D. White. In the Branch of the Chemistry (and Microscopy) of Food and Drugs, Fertilisers and Feeding Stuffs, Soils, and Water—J. H. Christie, B.Sc. (Lond.); and C. G. Collins. Two candidates examined at Johannesburg have also satisfied the Board:—In the Branch of Metallurgical Chemistry, D. Millin, B.A. (Cape); and in the Branch of Organic Chemistry, A. Kloot, B.Sc. (Lond.).

THE CHEMICAL NEWS

VOL. CX., No. 2854.

THE DETERMINATION OF THE LIME REQUIREMENTS OF THE SOIL.

By H. B. HUTCHINSON and K. MACLENNAN,
Rothamsted Experimental Station.

THE use of lime as a means of soil amelioration has been recognised by agriculturists since the time of the early Romans. Its application as marl, shells, chalk, limestone, and burnt lime is recorded in all the earlier books on British agriculture, and, in fact, the practice persisted until well into the nineteenth century. With the incidence of low prices, bad seasons, and an increasing appreciation of the value of the more quickly acting artificial manures, the practice fell into abeyance some thirty years ago, and since that time not only British but also some of the Continental agriculturists have been living on the heritage left by their predecessors.

Within this period, however, and with the growth of agricultural science, it has become increasingly apparent from physical, chemical, and biological considerations that a resumption of the practice was, in many cases, of paramount importance if the fertility of the soil was to be maintained. Notably on the Continent, where large tracts of peaty moorland are to be found, the primary importance of lime as an agent in the reclamation of virgin soils was constantly demonstrated, whilst conditions in the eastern states of America were equally indicative of lime starvation.

It is natural, therefore, that repeated attempts should have been made to determine the lime requirements of the soil, and of these two chief lines of inquiry may be mentioned. The first consists of the application of lime in various amounts and in different forms to field plots under controlled conditions, whereas the second is represented by the introduction of chemical and other methods to indicate the requirements of any given soil. Whilst attention in Britain has been almost entirely confined to the former type of investigation, much work has been done in Germany and the States in the latter direction, and in Denmark in recent years the results of laboratory methods have been advantageously correlated with conditions actually obtaining in the field.

Although the maintenance of a favourable soil reaction and the neutralisation of the acids formed by biological processes in the soil is secured by means of a solution of calcium carbonate in the soil water, the methods proposed for the determination of the lime requirement of acidity of the soil have rested on a great diversity of chemical reactions, qualitative and quantitative.

The obvious but rough test for soil reaction is the commonly adopted litmus-paper test, and this has been extended by Christensen and Larsen to litmus solution, varying tints produced being taken as a rough measure of the acidity (*Tidskrift for Landbrugets Planteavl*, 1910, xvii., 407, and *Centr. Bakt. Par.*, [II.], 1911, xxix., 358). Loew advocates the use of a solution of potassium iodide and starch as being roughly quantitative (*Zeit. für Landw. Vers. Wesen in Österreich.*, 1909, 462).

Numerous methods based on the determination of calcium as carbonate or other salts soluble in dilute acids or salt solutions have been suggested. The importance of a definite amount of calcium carbonate has been strongly urged by English agricultural writers on the assumption that the only effective compounds for soil purposes is the carbonate, and the minimum content has often been placed at 0.2 to 0.5 per cent. There is no doubt, however, that this is too high, but comparison with Continental standards is rendered difficult by the lack of uniformity in

the methods of determination; although it has been frequently shown that treatment of the soil with boiling acids gives rise to the production of carbon dioxide other than that derived from carbonates, this method is still largely practised.

As distinct from these may be mentioned the estimation of lime soluble in various organic and inorganic acids and neutral salts. Kellner suggested a method (*Landw. Vers. Stat.* 1887, xxxiii., 359), afterwards largely adopted by Meyer (*Landw. Jahrb.*, 1900, xxix., 913), in which the soil is exposed to the action of a solution of ammonium chloride. While the data thus obtained have been of distinct use in many cases there have been others in which the results were directly contradictory, and in further extensive experiments Meyer expresses the opinion that the determination of the acidity of the soil must receive much more attention than has hitherto been the case (*Landw. Jahrb.*, 1910, xxix., *Erganz. Bd. III.*, 287. Christensen and Larsen (*loc. cit.*) also found by correlation of the results obtained from the ammonium chloride method with those in the field, that with 49 out of 116 soils little guidance could thus be acquired.

Holleman proposed extraction of the soil with water saturated with carbon dioxide and estimation of the lime removed (*Landw. Vers. Stat.*, 1892, xli., 38). Sulphuric acid (Immendorf, *Fifth Intern. Cong. App. Chem.*, Berlin, 1913, III., 740), acetic acid, dilute and concentrated hydrochloric acid have also been used, and have given rise to the creation of standards often without value.

Whereas the above are based on the presence of certain lime compounds, the determination of the lack of bases or soil acidity has been more or less followed. Tacke introduced a method depending on the amount of carbon dioxide evolved from an excess of finely precipitated calcium carbonate (*Chem. Zeit.*, 1897, xxii., 174), while in Süchting's modification of this a definite amount of chalk is added (*Zeit. Angew. Chem.*, 1908, xxiii., 151), and the residual carbonate existing after a certain period is estimated.

The capacity of soil acids to displace mineral acids from neutral salts has been employed by Hopkins, Knox, and Pettit by means of potassium nitrate solution (*Proc. 19th Ann. Conv. Off. Agric. Chem.*, Washington, 1902). The reaction was found to be extremely tardy, and the results obtained by successive portions of solution were in decreasing geometrical progression, and for the interpretation of the results a factor is used. Loew (*Bull. 13, Porto Rico Agric. Exp. Stat.*, 1913, 7), and also Jones (*American Fertiliser*, 1913, xxxix., 29), employ a solution of a neutral acetate for the same purpose, but from results obtained by us it seems apparent that this method is open to the same objection as the preceding one. Gregoire, Hendrick, Carpiaux, and Germain (*Ann. Stat. Agron. Genbloux*, 1913, ii., 87) have recently investigated the action of soils on "Kjeldahl's solution" consisting of potassium iodide, iodate, and sodium thiosulphate, and the examination of a very large number of soils has permitted of differentiation according to intensity of action, although neutral soils were also found to give a distinctly positive reaction.

Methods involving the use of alkaline solutions such as ammonia have been used by Müntz (Frémy's "Encyclopédie Chimique," iv., 182), and Wheeler, Hartwell, and Sargent (*Journ. Am. Chem. Soc.*, 1900, xxii., 153), barium hydroxide solution was employed by Albert (*Zeit. Angew. Chem.*, 1909, xxii., 533), and Lyon and Bizzell (*Journ. Ind. and Eng. Chem.*, 1913, v., 12), whilst calcium hydroxide was used by Wheeler and his colleagues and by Veitch (*Journ. Am. Chem. Soc.*, 1902, xxiv., 1120).

The method proposed by the latter has found fairly wide adoption in the United States, and gives, as far as our own experience goes, results closely approximating to the actual. It is, however, a very tedious process, and is difficult of adoption on a large scale.

In the course of other work on the action of lime on the

fertility of the soil, which has been carried out in this laboratory, the need was felt of a simple and accurate method for the determination of the lime requirement of the soil. Attention has already been called to the general view that carbonates and bicarbonates are the chief compounds tending to maintain a neutral reaction of the soil, and to these certain easily hydrolysable calcium and other silicates may be added. It appeared, therefore, that a closer investigation of the action of certain carbonates on the soil might give a measure of prevailing acidity, and would possibly conform more closely to natural conditions than some of the compounds hitherto employed.

Preliminary work with sodium carbonate and bicarbonate gave unsatisfactory results, inasmuch as the deflocculation of the clay compounds of the soil occurred, and adversely affected the rate of filtration; a coloured extract difficult of titration was also obtained, and, furthermore, these compounds were found to give positive absorption even in the case of neutral soils containing abundance of calcium carbonate initially. Recourse was then had to the use of a solution of calcium bicarbonate, and after minor modifications, as to period of digestion, strength of solution, &c., this method has been used with a large number of soils under well controlled conditions.

The solution may be prepared by passing a current of carbon dioxide into a suspension of calcium carbonate in distilled water, or by means of a "Sparklet" or refillable soda-water syphon, where bulbs of compressed carbon dioxide are used. The latter method is the more convenient, and permits of the preparation of a saturated solution within quite a short time. A large excess of carbonate must be used in order to provide an abundance of small particles which readily pass into solution; the contents of the syphon may be diluted with one-third its volume of distilled water before filtering, and this will result in the formation of a solution of approximately N/50 strength.

For a determination of acidity, or lime requirement, 10–20 grms. of the soil are placed in a bottle of 500–1000 cc. capacity together with 200–300 cc. of the approximately N/50 solution of calcium bicarbonate, and the air in the bottle is displaced by a current of carbon dioxide in order to insure against possible precipitation of the calcium carbonate during the period of determination. The bottle is then placed in a shaking machine for three hours, after which time it is opened, the liquid is filtered, and a portion of the filtrate equal to half of the original amount of bicarbonate solution is titrated against N/10 acid, using methyl orange as indicator. The difference between this final titration and that of the initial solution represents the amount of calcium carbonate absorbed, each cubic centimetre of N/10 acid being equal to 5 mgrms. calcium carbonate.

This method has been tested within the last few months on a number of different soils, the behaviour of which has been ascertained bacteriologically and chemically in the laboratory. A few of these results are summarised in Table I., in which the production of ammonia and nitrates and plant growth in untreated and limed soils is given.

TABLE I.—*The Relation between Soil Acidity, the Production of Ammonia and Nitrates, and Plant Growth in certain Soils.*

Soil.	Lime req. as per cent CaCO ₃ .	Increase in ammonia and nitrates (pts. per mill. dry soil).		Plant growth (production of dry matter in 4 crops).	
		Unt. Soil.	Soil CaCO ₃ .	Unt. soil.	Soil. CaCO ₃ .
Rothamsted ..	Nil	7	6	100	105
Chelsea ..	Nil	49	44	100	99
Millbrook ..	0.02	7	12	100	97
Woburn ..	0.26	40	84	100*	740*
Craibstone ..	0.43	26	47	100	144

* From other experiments, first crop only.

The two soils, Rothamsted and Chelsea, contained initially an abundance of carbonate (2.6 and 0.8 per cent

respectively), and the further addition of chalk gives returns varying only slightly from those of the control soils; Millbrook soil, which is almost neutral, gives a slight increase in nitrates and a depression in plant growth. The two acid soils, Woburn and Craibstone, respond readily to chalk applications, as indicated by increased nitrate production and plant growth of the first four crops after treatment.

During the investigations mentioned above, other portions of the same soils were treated with increasing amounts of calcium oxide, and allowed to stand in a moist condition for about twelve months. These have now been examined by this method in order to ascertain how far the original reaction had been affected by the application of such doses. The results are given in Table II., where the acidity is given in terms of calcium carbonate required to neutralise the soil in each case.

TABLE II.—*The Acidity of Certain Soils after Treatment with Lime.*

CaO applied (stated as CaCO ₃ per cent).	Rothamsted.	Millbrook.	Woburn.	Craibstone.
0	0	0.05	0.26	0.43
0.18	0	0	0.20	0.27
0.36	0	0	0.05	0.08
0.54	0	0	0	0.02
0.72	0	0	0	0

Further pot culture experiments have been made with an acid soil to which definite amounts of calcium carbonate were supplied, and the crop results obtained show quite unmistakably that the acidity indicated by the above method coincides with the physiological gauge set by the plant. The crop growth was found to increase directly with increasing applications of carbonate until the neutral point was reached, and then, with increasing carbonate, remained constant.

In addition to its value for practical agricultural work, the method will possibly be of use in various ecological problems, where the relations between plant and soil require more accurate determination.

OSMIUM-PLATINUM—A NEW ALLOY.*

By F. ZIMMERMANN.

OF the several metals of the platinum group platinum, palladium, iridium, and rhodium have been most generally employed in the industrial arts, either alone or in combination as bivalent alloys. Of the latter, iridium-platinum is the best known, but the growing scarcity of iridium has led to the search for other combinations of the metals of this group yielding alloys possessing physical and chemical properties of equal if not greater value. The rarer metals of the platinum group are not easily obtained in great purity, and because of this fact but little success has heretofore been obtained when combining them as bivalent alloys. Furthermore, the strong affinity of osmium for oxygen has increased the difficulty of making alloys of it with other metals in definite proportions. After much experimentation by the author, highly refined platinum and osmium have been successfully combined in widely varying proportions yielding alloys of commercial value. While the two metals may be combined in almost any proportion, alloys containing from 1 to 10 per cent of osmium and 99 to 90 per cent of platinum are chiefly used.

Great purity of the components is essential, as the presence of small percentages of other elements appears to be very detrimental to the properties of the resulting alloy. According to the chemical and physical behaviour, it seems that one part of osmium in an alloy with platinum will take the place of two and one-half times its weight of

* Paper presented at the Twenty fourth General Meeting of the American Electrochemical Society, at Denver, Colorado.

iridium. The osmium-platinum alloy is very acid-resisting, and for this reason may be of great service in the electro-chemical industry. Its electrical resistance is considerably higher than that of an iridium-platinum alloy of the same percentage composition. The alloy further possesses great hardness and tensile strength. Wires of the finest size are drawn with comparative ease.

A thorough study of the alloy is in progress, and definite results of tests may be of sufficient interest for a later paper.

The alloy has been patented—U.S. Patent No. 1,055,199, March 4, 1913.—*Chemical Engineer*, xviii., No. 3.

THE CHEMICAL SIGNIFICANCE OF CRYSTALLINE FORM.*

By THEODORE W. RICHARDS.

(Concluded from p. 53).

TURNING now once more to the compound containing 1 atom of hydrogen, we see here great difference in crystal form. This is also just what we should expect in a compressible system, provided that the newly introduced member of the system possessed not only a different molecular volume, but also a different chemical nature. Under such circumstances a marked change in the habit and a twisting distortion of the symmetry might very well be supposed to occur.

The axial ratios in the camphor series presented by Barlow and Pope a few pages afterward show somewhat the same sort of treatment. The first point that strikes one upon comparing the figures is that hexagonal camphor and its orthorhombic substitution products are very different from one another in their actual crystal forms and that the dibromcamphors differ much among themselves. Barlow and Pope have been interested in devising a mathematical method which should reconcile these figures; but if the method had been less arbitrary, it would have been more convincing. In order, for instance, that the orthorhombic dibromcamphors may be reconciled at all with hexagonal camphor, arbitrary multiples of the axes must be chosen, one of them being as complicated as $5/3$. One cannot but wonder if any similarity in crystalline form would have been detected between these substances if one had not happened to know beforehand that they had a similar structure. Grave doubts may well arise as to the legitimacy of turning away thus from the indication of the actual external crystalline forms.

It will be clear from the foregoing statements that the interest of these investigators has been primarily to show analogies of crystal form. While this is very suggestive, to me the differences seem to be even more interesting than the analogies; for the differences give us a clue whereby further insight into the internal nature of crystals may be obtained.

There are many other cases of approximate similarity of form, where it is hard to see how Barlow and Pope's theory may be made to apply; for example, the interesting series of nitro-dihalogen benzenes recently studied by E. Repossi (*Zeit. Kryst. Min.*, xlv., 202; through *Chem. Zentralb.*, 1909, xi., 273). A table giving the axial ratios of four of these compounds follows:—

1-Nitro-2, 5-dibromo benzene ..	1'3854 : 1 : 0'7876
1-Nitro-2-chloro-5-bromobenzene	1'3823 : 1 : 0'8106
1-Nitro-2-bromo-5-chlorobenzene	1'4159 : 1 : 0'8157
1-Nitro-2, 5-dichloro-benzene ..	1'4385 : 1 : 0'8223

It will be noted that there is a very distinct difference in the fundamental axial ratios of these four highly analogous substances, amounting to several per cent. Clearly the introduction of chlorine causes a relative shortening of the axis *b* even more evident than that shown in the substituted

ethanes. How this decided distortion could be accounted for on the hypothesis proposed by Barlow and Pope it is difficult to see. On the other hand, the flexibility of interpretation allowed by the theory of compressible atoms is amply sufficient to account for just this sort of thing.

Similar small but significant differences in isomorphous crystal shapes are pointed out in a recent interesting paper by B. Gossner (*Krystallographie*, xlv., 417). Here again the evidence that in isomorphous mixed crystals the two components mutually influence each other in such a way that their properties are no longer those of the pure state is an outcome which might have been definitely predicted from the point of view of the theory of compressible atoms.

The data presented by Groth's "Chemische Krystallographie" (Engelmann, Leipzig) concerning not only inorganic but also a great variety of organic substances will enable anyone interested to test for himself these statements. In general, it will be seen, as has been pointed out above, that the rigid application of the theory of definite valency-volume is impossible and that according to it many facts such as those given in Repossi's table above are inexplicable.

The cases cited by F. M. Jaeger (*Journ. Chem. Soc.*, 1908, xciii., 517) in favour of the Barlow-Pope theory may be used (in so far as they show significant parallelism) equally well to support the theory of compressible atoms. The two theories are similar, as had already been pointed out, in the ideas of close-packing and definite marshalling. Hence in these and in other cases the arguments with regard to these two matters apply about equally to each; but when Jaeger calls the crystals of phthalimide and saccharin closely similar in form, one cannot help thinking that the argument is somewhat far-fetched.

Here follow the actual crystallographic data:—

	$a : b : c.$	$\beta.$
Saccharin 	$SO_2 \rangle NH$	1'356 : 1 : 0'430; (94°3')
Phthalimide 	$CO \rangle NH$	1'491 : 1 : 0'497; (91°18')

These marked differences in axial ratios, amounting to 10 per cent in the case of *a*, must correspond with real differences in internal conditions; the extra oxygen in saccharine and the substitution of sulphur for carbon are by no means unimportant matters. The method of "equivalence parameters" reduces these data to much closer agreement; thus *x*, corresponding to the axis of *a*, is found to be 2'518 in one case and 2'462 in another. The difference is only about 2 per cent instead of 10. Such a circumstance cannot convince me that the crystals are to be considered as alike; I am more inclined to believe that the outcome gives evidence of the efficiency of the mathematical method in hiding real differences in crystal forms.

Jaeger's earlier statement that the Barlow-Pope theory is not to be regarded as affording an explanation of valency, nor as a substitute for the theory of structure of organic chemistry, nor as furnishing an indication of the occurrence or non-occurrence of miscibility among solid phases, seems to have more justification. The single advantage cited by Jaeger, that the Barlow-Pope hypothesis enables one to predict similarities in crystalline form, would apply equally well to any reasonable theory involving definite close-packing of the spheres of influence, if some elasticity in these spheres is allowed—and the facts seem to demand the admission of the existence of this latter property.

Many other cases are considered by Barlow and Pope, some of them with great ingenuity, and all with profound

* *Journal of the American Chemical Society*, xxxv., No. 4.

knowledge of crystallography. Some of the arrangements are very plausible, but most of them would hold quite as well if not better according to several other hypotheses as to the relative volumes of the several atoms, especially if we take into account atomic compressibility. The explanation for the similarity in crystalline form of sodium nitrate and calcium carbonate is especially interesting and ingenious, because, according to their theory, the former has a different total valency-volume from the latter. This similarity also can be explained in other ways than on their basis. The well-known older explanation, supposing the similarity of form to be due to the fact that the two molal volumes are almost identical and the number of atoms in each the same, is quite as convincing as Barlow and Pope's more elaborate theory (*Journ. Chem. Soc.*, 1908, xciii., 1528). Indeed this older explanation fits in very well with the idea defended by the present paper; for the attribute of atomic compressibility is all that is needed to explain the indisputable fact that two somewhat differently combined but otherwise analogous groups of atoms of approximately but not exactly equal bulks can be pressed into very similar forms.

There are other cases of isomorphism which seem to be wholly beyond the reach of the valency-volume theory of Barlow and Pope—for instance, the familiar isomorphism of ammonium and potassium salts. Here the idea of valency-volume gives ammonium nine volumes, but potassium only one; and it is hard to see how any sort of analogous symmetry could be constructed in the two cases under these circumstances. On the other hand the theory of compressible atoms plausibly suggests that the five atoms making up the radical ammonium, which seem together to possess about the same volume as potassium (the molal volumes of potassium and ammonium chlorides are respectively 37.8 and 35.0 cc.), must be compressed by their mutual affinities until a shape not unlike that occupied by the compressed and distorted potassium is obtained.

It is very questionable if at present there is any use in attempting to make models of the molecules of very complex substances, in view of the many variables which seem to exist within their structure. Because of the fact that sometimes exceedingly complicated structures, such as crystallised ammonium alum, assume very simple crystallographic forms, one is inclined to proceed cautiously with them in his attempt to represent pictorially the actual arrangement of the atoms in a crystalline structure.

Nevertheless, it seems clear, at least to the writer, that the tenets of the theory of compressible atoms give the most reasonable point of attack in a research of this kind. For the theory not only postulates causes which do not seem to be at variance with common sense, but it also gives just that sort of flexibility in atomic volumes and in the mutual adjustment of the effects of the several affinities which seems to be indicated by the slightly differing angles and the varying relations of isomorphous but not exactly identical crystalline forms.

Summary.

In this brief paper the following points are emphasised:—

1. The assumption of valency-volume made by Barlow and Pope in 1906, in spite of its great ingenuity, is shown to be not the most reasonable explanation for the actual molecular volumes of solids.

2. The cases presented by them as arguments may be explained quite as well (or often better) in other ways, and therefore afford no arguments in favour of their assumption as against others.

3. Some facts seem to be quite beyond the reach of their hypothesis.

4. In 1902 the theory of compressible atoms indicated a more reasonable method of explaining the tridimensional relations of material, including the symmetry of crystals.

5. This theory assumes, like Barlow and Pope's later

hypothesis, the close packing of the atoms in solids, whereby the form is maintained and the rigidity caused. It proposes, however, that the atoms are compressible and that their volumes are not arbitrary, but depend upon the pressure to which they are subjected.

6. The theory of compressible atoms explains the usual forms of elements and binary compounds better than Barlow and Pope's.

7. The theory shows why elements forming isomorphous compounds need not have exactly the same atomic volume.

8. The theory affords a conceivable picture as to how potassium and ammonium can replace one another isomorphously, a problem apparently beyond the reach of the hypothesis of constant valency-volume.

9. In general, none of the facts cited by Barlow and Pope, and no other crystallographic facts known to the author, conflict with the postulate of atomic compressibility.

10. Complex compounds possess too many variables for satisfactory treatment at present; but in so far as interpretation is possible, the theory of compressible atoms seems to apply.

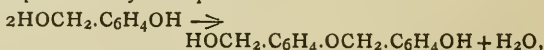
SYNTHETIC RESINS.*

By L. V. REDMAN, A. J. WEITH, and F. P. BROCK.

Condensation Products of Phenolic Bodies with Hexamethylene Tetramine.

THE condensation products or synthetic resins which occur when phenolic bodies are heated in a water solution of formaldehyde, their polymers or equivalents, are already well known from scientific and patent literature. The term "phenolic bodies" signifies any substance containing a benzene nucleus and having a hydroxyl attached to the ring, *e.g.*, the cresols, naphthols, thymol, carvacrol, &c., the chlor- and brom-phenols, nitro-phenols, phenol sulphonic acid, &c. The term formaldehyde includes its hydrates or polymers and may be replaced in the reaction by acetaldehyde benzaldehyde, &c., in certain cases, but the formaldehyde is in every case more reactive than the substituted aldehyde or the aldehydes higher in the series.

The formaldehyde-phenol reaction products are formed in every case with the elimination of water as a by-product. The first step in the reaction goes according to the following equation:— $\text{C}_6\text{H}_5\text{OH} + \text{CH}_2\text{O} \rightarrow \text{HOCH}_2\text{C}_6\text{H}_4\text{OH}$, forming oxybenzyl alcohol. The second change may be represented by the equation:—



in which two molecules of oxybenzyl alcohol unite with the elimination of water and the formation of saligeno-saligenin. Further reaction may occur in which the saligenin molecules unite, forming a saliretin product with the further elimination of water.

The water of reaction is not the only water present, since commercial formaldehyde is 60 per cent water, and in the process of formation this water separates out from the newly formed resin.

The wet process for obtaining the synthetic resins has been exploited successfully, commercially, by a number of research chemists who have patented the results of their researches.

Difficulty is experienced in following the rate of this wet reaction, for, heretofore, phenol has been difficult to determine in the presence of formaldehyde, and formaldehyde requires a considerable length of time (about forty-eight hours) for each determination, the results being unreliable within 2 or 3 per cent. Consequently, great

* *Journal of Industrial and Engineering Chemistry*, vi., No. 1.

difficulty is experienced in following the progress of the condensation.

An attempt has been made by Jablonower (*Journ. Am. Chem. Soc.*, 1913, xxxv., 811) to follow the velocity of this reaction in an open system by measuring the rate of change in the specific gravity of the reacting mixtures.

The reaction between a phenolic body and formaldehyde or a polymer is only a part of the more general reaction which takes place between a simple or substituted mobile methylene group and any substance containing in its molecule a benzene nucleus to which a hydroxyl is generally attached.

The hydrogen of the active methylene group may be substituted by the alkyl radicals, giving the higher aldehydes of the fatty series or by a benzene nucleus giving the aromatic aldehydes. The oxygen, to which the active methylene group is attached, in aldehydes, may be replaced by sulphur or nitrogen. With sulphur the malodorous thio-aldehydes are formed; the nitrogen forms with active methylene groups hexamethylene tetramine, hydro-benzamide, &c. The nitrogen compounds are colourless, odourless, transparent, and crystalline, easily soluble in water, and sparingly soluble in alcohol. They sublime without melting, and are stable products; when boiled in dilute acids they break down into ammonia and the corresponding aldehydes; boiling in alkali has no effect upon them.

Hereafter, the word phenol will be used to designate all compounds having a hydroxyl group attached to the benzene nucleus, and by the term "methylene body" shall be understood all compounds containing an active methylene group; the hydrogen of the group may or may not be replaced by other bodies or radicals, and the methylene group may be attached to oxygen, nitrogen, sulphur, or their equivalent which allows the methylene to remain active.

HISTORICAL.

Condensation of the Salicylates.

As early as 1853 Gerhardt (*Ann. der Chemie*, 1853, lxxvii., 159) showed that an insoluble resin could be produced by the dehydrating of sodium salicylate by means of phosphorus oxychloride, giving as the reaction $2(C_7H_6O_3) \rightarrow C_{14}H_{10}O_5 + H_2O$. Gerhardt notes that this resin will hydrolyse in KOH solution.

Schroder, Prinzhorn, and Kraut (*Ibid.*, 1869, cl., 1) in 1869 by dehydrating sodium salicylate with $POCl_3$ produced a resin insoluble in water, alcohol, ether, &c., which hydrolysed back in the presence of KOH to salicylic acid. Combustion of the insoluble resin gave:—

	C	H.
Obtained by Socoloff	68.94	3.64
Obtained by Prinzhorn	68.92	3.44
Calculated for heptasalicylo-salicylic acid	68.71	3.48
Calculated for octosalicylo-salicylic acid..	68.85	3.46
Calculated for nonosalicylo-salicylic acid	68.92	3.44

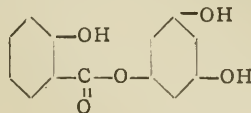
The calculations show for the octo- and nonosalicylo-salicylic acid a better agreement with the combustion experiments than does the calculated value for heptasalicylo-salicylic acid. This larger molecular chain agrees with the results of Beilstein and Seelheim in dehydrating saligenin as re-calculated (see below).

The probable linking of the chain is according to the formula $HO.C_6H_4.COO.(C_6H_4.COO)_7.C_6H_4.COOH$.

Velden in 1877 (*Jahresberichte*, 1877, v., 37) showed that salicylic acid, in the presence of sodium amalgam and acid, would reduce to an oxybenzylalcohol and then dehydrate into a saliretin body. This same phenomenon has been shown by Dr. Baekeland (*Journ. Indust. and Eng. Chem.*, 1912, iv., 737) to be possible when salicylic acid is reduced at the cathode by electrolysis.

Salicylic acid and pyrogallol boiled in absolute alcohol give a product which is soluble in alcohol, has the formula $(C_{26}H_{22}O_9)$, and is probably represented (Paterno,

Gazzetta Chem. Italiana, 1872, ii., 1) by a dehydrated polymer of—



Condensation of Phenols and Higher Aldehydes.

In 1871 Baeyer (*Ber.*, 1871, v., 25; 1872, v., 280) showed that benzaldehyde and pyrogallol gave a substance insoluble in KOH, the reaction going according to the equation $2(C_7H_6O) + 2(C_6H_6O_3) = (C_{26}H_{22}O_7) + H_2O$. The resin thus produced reddens on oxidising, and bleaches on reducing, and by heating at 200° C. passes with the loss of hydrogen to a substance of the formula $C_{26}H_{16}O_7$.

Phenol and benzaldehyde, with H_2SO_4 as the condensing agent, give a red resin which was soluble with a red colour in concentrated sulphuric acid, water, or alkali, and gives in alkali a beautiful violet colour.

Formaldehyde, phenol, and concentrated sulphuric acid give a pasty mass which dissolves in KOH solution.

Trzcinski in 1884 (*Ber.*, 1884, xvii., 499) working with benzaldehyde and β -naphthol, produced a resin which is insoluble in alkalis, and which may be represented by $4C_{10}H_8O_4.C_6H_5.CHO-(5H_2O)$.

In 1886 Claus and Trainer (*Ber.*, 1886, xix., 3004) showed that aldehydes and ethyl alcohol condensed with HCl gave alkali insoluble products. They showed further that by boiling 2 mols. of phenol and 1 mol. of acetaldehyde in ether a substance was formed which resembled very closely a higher saliretin in its qualities and gave as its possible formula $H_2C(C_6H_4OH)_2$; β -naphthol and acetaldehyde in HCl, gave products insoluble in KOH, while α -naphthol gave a resin soluble in alkali. Their formula suggested for β -naphthol resin is $C_{24}H_{18}O_2(C_{10}H_7)_2$ and for the α -naphthol resin $C_{24}H_{18}O_2(C_{10}H_6OH)_2$.

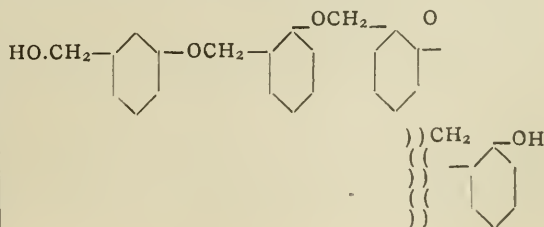
Condensation of Oxybenzyl Alcohols (Saligenin).

Beilstein and Seelheim in 1861 (*Ann. der Chemie*, 1861, cxvii., 87) produced a resin from oxybenzylalcohol by dehydrating this substance with acetic anhydride or ethyl iodide, which on analysis gave:—

	C.	H.
Experiment 1.. .. .	78.02	5.98
Experiment 2.. .. .	77.44	5.93
Experiment 3.. .. .	77.80	5.60
Calculated for $8C_7H_8O_2-7H_2O$..	77.59	5.77

and Kraut (*Ann. der Chemie*, clvi., 123) in reviewing this work suggests the formula $C_{56}H_{50}O_9=8(C_7H_8O_2)-7H_2O$, which he names heptasaligeno-saligenin. That would be for a substance where $C=77.59$, $H=5.77$, which agrees fairly well with results for Expt. 2; but Expt. 1 agrees better with $11(C_6H_8O_2)-10H_2O=C_{77}H_{68}O_{12}$, since for this formula $C=78.02$, $H=5.74$; and Expt. 3 may be represented by $9(C_7H_8O_2)-8H_2O=(C_{63}H_{56}O_{10})$, where $C=77.77$, $H=5.76$.

From these results it seems not unreasonable to conclude that the insoluble resin formed is variable, and is formed by simply lengthening the molecular chain and may proceed indefinitely. The chain of the type—



continuing to grow indefinitely. The longer the chain the more nearly will the proportions of phenyl to the methylene group be 1 : 1.

Moitessier (*Jahresberichte*, 1866, p. 677), in 1866, pointed out that saligenin dehydrated and with the loss of one water passed over into a saliretin resin.

Condensation of Benzene Nuclei and Formaldehyde.

As early as 1871 Baeyer (*Ber.*, 1871, v., 25; 1872, v., 280) published a monograph on the condensation of phenols with aldehydes in which he concludes "Dass sich alle aldehyde mit allen Phenolen zu Körpern verinigen." And Manasse in 1894, working with synthetic resins made from phenols, notes that "Es ist keine neue Beobachtung das beide Componenten in Verhältnisse 1 : 1 zusammenzutreten."

Baeyer (*Ber.*, 1872, v., 280) demonstrated also that formaldehyde could be replaced by chloral or the ammonia aldehydes in water and that the phenols such as pyrogallol, resorcin, benzoic acid, gallic acid, &c., would act similarly to phenol.

Schotten (*Ber.*, 1878, xi., 784), in 1878, produced resinous substances with formaldehyde and phenols in which the hydrogen of the ring was replaced by such groups as $-\text{CH}_3$, $-\text{NO}_2$, $-\text{COOH}$, &c.

Tollens (*Ber.*, 1884, xvii., 653), in 1874, produced a rather remarkable product from the reaction of formaldehyde on aniline according to the reaction $\text{C}_6\text{H}_5\text{NH}_2 + \text{CH}_2\text{O} \rightarrow \text{C}_6\text{H}_5-\text{N}=\text{CH}_2$.

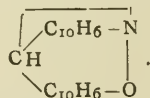
In 1891 Kleeberg (*Ann. der Chemie*, cclxiii., 283) made a resin by adding 10 grms. phenol to 20 cc. formalin and adding, further, with cooling, concentrated HCl. The result was a resin insoluble in alkali, and from this purified resin he could obtain no concordant combustion analysis.

With gallic acid and formaldehyde a substance $\text{C}_{16}\text{H}_{13}\text{O}_{10}$ was obtained.

Abel (*Ber.*, 1892, xxv., 3477), in 1892, made from α - and β -naphthol and formaldehyde, in acetic acid, soluble resins which, on treating with alkaline halogens, became quite insoluble, going over to the substance—



which could be readily reduced with zinc dust in acid solution. Treating the dinaphthol methanes with hydroxylamine produced an insoluble substance—



Abel also pointed out that thymol and guaiacol gave condensation products.

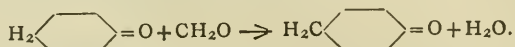
In 1892 Hosaeus (*Ber.*, 1892, xxv., 3213) showed that phenol, resorcin, pyrogallol, or phloroglucin heated with dilute formalin in the presence of rather strong H_2SO_4 or HCl gave insoluble resins.

Manasse, 1894, produced a resin by taking—

- 1 mol. phenol
- 1 mol. 40 per cent formalin
- 1 mol. caustic soda

and allowing the reaction to take place in the cold; the odour of formaldehyde disappears, and orthoxybenzyl alcohol is the chief product.

Wohl and Mylo (*Ber.*, 1912, xlv., 2046), in 1912, working with acrolein, suggest the polymerisation of formalin and phenol according to the equation—



That this does take place to a certain extent may account for the quinone colouring of the resins, being green in alkali and red in acid.

Lebach (*Zeit. f. Angew. Chemie*, 1909, xxii., 1598; *Journ. Soc. Chem. Ind.*, 1913, xxxii., 559) (1909—1913) deals at length with the application of these resins to specific industries. The resins are produced in every case from the boiling together of phenols and aqueous formaldehyde in the presence of a condensing agent.

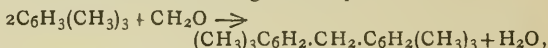
Dr. Baekeland (*Trans. Am. Electrochem. Soc.*, 1909, xv., 149; *Journ. Ind. and Eng. Chem.*, 1909, i., 149, 545; 1911, iii., 932; 1912, iv., 737; 1913, v., 506) has published a number of original papers on the practical application of these resins which are formed from aldehydes and phenols. A great variety of commercial articles has been produced by the use of these resins as binders, glues, lacquers, varnishes, shellacs, and solid products imitating amber, horn, bone, vulcanised rubber, &c. He showed that this reaction, which is too violent when large quantities of catalysts are added, and too slow as a rule when no catalyst is present, may be controlled effectively by adding less than one-fifth of a formula weight of a basic substance for each mol. of phenol present. He pointed out also that the resins formed when a basic substance is present are more insoluble in ordinary solvents than those resins formed in the presence of acids.

Litterschied and Thimme (*Chem. Centr.*, 1904, Bd. 949), in 1904, produced insoluble phenolic resins by substituting monochlor methyl ether, $\text{ClCH}_2-\text{O}-\text{CH}_3$, for formaldehyde.

Condensation of Aromatic Hydrocarbons and Formaldehyde.

A very remarkable polymerisation (Baeyer, *Ber.*, 1872, v., 1094) takes place when mesitylene (symmetrical trimethylbenzene) is treated with formaldehyde, glacial acetic acid, and concentrated sulphuric acid.

The reaction is according to the equation—



and this substance is always formed no matter what proportions of the original substances are used.

A similar reaction takes place when benzene and chloral react according to the equation—



which yields diphenyl trichlor ethane. This remarkable condensation of benzene nuclei with methylenes in the absence of hydroxyls was noted by Baeyer "Es scheinen sich überhaupt alle Aldehyde unter geeigneten Umständen direkt mit den aromatischen Kohlenwasserstoffen zu verbinden in dessen treten dabei häufig Harze auf."

Patent Literature.—For fifteen years efforts have been made to commercialise these synthetic phenolic resins. Smith (Brit. Pat. 16,247, 1899; Ger. Pat. 112,685, 1899), in 1899, patented a product and process obtained by heating 1 mol. of phenol with 1 mol. of formaldehyde and strong HCl, adding wood alcohol and amyl alcohol to retard the reaction. The material was then dried in sheets at 100° C. for twelve to thirty hours.

Luft (Ger. Pat. 140,552, 1902; U.S. Pat. 735,278), in 1902, in his improved process added such substances as glycerin and camphor to make the synthetic resins more suitable for moulding.

Blumer (Brit. Pat. 12,880, 1902), in the same year, produced a resin suitable as a shellac substitute by using tartaric acid in large amounts as a condensing agent, e.g., 2 mols. of phenol, 2 mols. of ormalin, and 1 mol. of tartaric acid.

Fayolle (Fr. Pat. 33,584, 1903; 2414, 1904; 2485, 1904; 341,013, 1904), in his French patents, uses sulphuric acid as a condensing agent, and adds large quantities of glycerin, pitch, oils, &c., as organic filters.

Story (Brit. Pat. 8875, 1905), in 1905, omitted condensing agents altogether; after boiling the phenol and formaldehyde for eight to ten hours at 100° C. the resin is dried out at 80° C.

In 1905 DeLaire (Fr. Pat. 361,539, 1905) introduced caustic as a condensing agent. He used the alkali in

equimolecular proportions with the phenol and precipitated the resin from solution by acid.

DeLaire (Brit. Pat. 204,811, 1907; Ger. Pat. 189,262, 1905) advanced the art further by resinifying phenol alcohols with heat and reduced pressure.

Fried. Bayer and Co. (Ger. Pat. 201,261, 1907), 1907, patented a process of making odourless shellac substitutes by using *o*-cresol in place of the ordinary phenols.

Helm (Brit. Pat. 25,216, 1907), 1907, introduced amines and ammonium salts as condensing agents or catalysts. The agents he uses in almost equimolecular proportions.

A series of patents were taken out in 1907 by Knoll and Co. in Germany and by Wetter in Great Britain for H. Lebach in which the condensing agents were acid or alkaline salts; sodium sulphite is especially mentioned (Brit. Pat. 28,009, 1907; 24,072, 1908; Swiss. Pat. 40,994, 1907; Fr. Pat. 395,657; Belg. Pat. 204,811, 1907). In Brit. Pat. 28,009, 1907, occurs the first mention of the possible use of hexamethylenetetramine. However, the patent text shows clearly that this reaction is no other than a water process to which a condensing agent has been added.

Grognot (U.S. Pat. 391,436, 1908), in 1908, patented a process for making phenolic resins in the presence of large quantities of glycerin, and after the reaction has proceeded the desired length distilling off the excess water and glycerin.

Dr. Baekeland has patented processes for producing synthetic resins from phenols and formaldehyde in the presence of less than one-fifth of a mol. of basic condensing agents per mol. of phenol (U.S. Pat. 939,666, 941,605, 942,699, 942,700, 942,808, 942,809, 942,852, 949,671, 954,666, 957,137, 982,230, 1,018,385, 1,019,406, 1,019,407, 1,019,408). The reaction may be kept well under control if the condensing agent be present in small amounts and the resins are ordinarily more insoluble if basic rather than acid-condensing agents be used.

Dr. Baekeland (U.S. Pat. 942,809, 1909) warns against the use of condensing agents in excess of one-fifth of a formula weight per mol. of phenol for two reasons: (1) the rapid increase in the reaction caused by large amounts of the condensing agent; (2) the trouble which the presence of the condensing agent may cause in the final product; for example, he warns us that "if a large amount of ammonia be used hexamethylene tetramine is formed which is a crystalline body of definite chemical composition." Further, "It is therefore essential that the proportion of base should not exceed certain definite limits, and the maximum permissible proportion has been found to be less than one-fifth of the equimolecular proportion of the phenolic body present. If larger proportions of base be used, there are formed in the mass such amounts of disturbing bodies as serve to render the product technically inferior or worthless for the purpose of this invention."

Other patents (U.S. Pat. 1,020,593 and 1,029,737) have been granted recently to Aylsworth in which the resin, resulting from the heating of 2 mols. of phenol and one mol. of formaldehyde, is hardened by heating in the dry by the addition of a sufficient amount of hexamethylenetetramine.

Problem.—From a review, then, of the scientific and patent literature it is evident that there remains to be studied the reaction and the products which are formed when hexamethylene tetramine is made to react in the dry condition with anhydrous phenol. All the previous literature has had to do with phenols and active methylenes in water solution to which condensing agents have generally been added. The quantity and kind of condensing agent has been shown by Dr. Baekeland to be of prime importance in these reactions. Mention of the use of hexamethylene tetramine as a substitute for formaldehyde has been made by Wetter (*loc. cit.*), but it is reasonable to presume, from the context of his patents, that it was to be used in a water solution and in the presence of a condensing agent. All these previous processes require the

freeing of the resin from the water contained in the 40 per cent formaldehyde solution and also the water which is a by-product of the reaction. The resins prepared in this way have also to be washed free of the condensing agent.

However, in the case of anhydrous phenol and dry hexamethylenetetramine, there is no water present in the ingredients. Neither is there any water formed as a by-product and no condensing agent is present, which must later be freed from the resins by washing. The only by-product is ammonia and it escapes readily on account of its volatility.

In the study of this anhydrous reaction the conditions are always under exact control and the reactions are definite and easily followed. The resins formed have very great commercial possibilities on account of their uniformity, chemical inertness, dielectric properties, mechanical strength, high refractive index (lustre), plasticity at certain stages, and the cheapness and supply of the raw materials from which these resins are manufactured.

(To be continued).

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

ANTIVENOMOUS VACCINATIONS.

Mdme. Phisalix is following up her researches concerning vaccines. M. Edmond Perrier, Director of the Natural History Museum, has presented to the Academy a new paper on the venomous saliva of the lizard of Arizona, the heloderm of which she has already indicated the effects on the viper, the hedgehog, and man. The distinguished physiologist has specially searched whether the entire venom, such as the animal inoculates it in biting, can be employed as a vaccine. She also tried to find out whether heat modifies its properties, and if cholesterine creates also against this venom, as it does against the venom of the aspic viper, a certain immunity. In order to solve these diverse questions, she has prepared as follows, four series of guinea-pigs. Those of the first series have received by interperitoneal injections, performed at intervals of six days, 2, then 3 mgrms. of whole or entire venom of the heloderm (weighed dry) in a solution of distilled water at 1000°. Those of the second series received the venom, previously heated to 80° during five minutes, which is the condition in which the venom of the viper loses its toxic properties and keeps its vaccinating ones. The guinea-pigs of the third series received the venom that had been kept boiling for five minutes, under which condition the venom of the viper loses even its vaccinating properties, whereas the venom of the lizard keeps its toxic properties intact. Lastly, the guinea-pigs of the fourth series have received two injections of 10 and 15 mgrms. of cholesterine in solution in ether. Six days after the last preparatory inoculation, all the guinea-pigs were tried by the injection of 5 mgrms. of whole venom, which dose is nearly twice as fatal for the guinea-pigs, and which, according to the approximations of Mdme. Phisalix, is also fatal for man in a few hours. The animals prepared with the whole venom and the cholesterine have all resisted; those that had received the heated venom all died, some of the second series, in less than two hours; those of the third series in four and five hours; that is to say, about ten hours in advance of the witness guinea-pigs. From these experiments Mdme. Phisalix concludes that the whole venom and the cholesterine vaccinate against the venom of the heloderm, and that consequently a bad bite may give immunity against a second accident, if it has not caused death previously. She likewise concludes that in the entire venom there are at least two active substances, one toxic, which resists ebullition, the other vaccinating, which is already destroyed at 80°. It is exactly the inverse of what is obtained by heating the venom of the viper. In

experiments that have already been begun, Mdme. Phisalix will fix the limits of the duration of the immunity obtained both with the venom and with the cholesterine.

DEATH OF THE JAPANESE VARNISH TREE.

Dr. Edmond Perrier has just analysed before the Academy of Sciences a work of M. Kienckal d'Herculaix, entitled "Correlation between the Death of the *Ailanthus*, commonly called the Japanese Varnish Tree, and the Disappearance of its Inhabitant the Silkworm (*Attacus Cynthia*). On the roots and the radicles of the *Ailanthus* certain galliform or tuberiform excrescences are developed, which, as far as their structure is concerned, may be compared to wens or knobs, and which cause the trees to waste away and finally die. The silkworms of the *Ailanthus*, natives of China but naturalised in Europe, feed on the leaves of these trees that are thus degenerating, and are attacked by a septicæmic affection which causes their death. The author of the above work deduces from his observations this conclusion:—A tree, the *Ailanthus*, introduced into Europe 150 years ago, and a species of Lepidoptera (*Attacus Cynthia*) its guest, have lived in liberty for the last fifty years; both considered as naturalised are struck with degeneration, disease, and death, the one bringing about the disease and disappearance of the other.

THE NEBULA ORION.

MM. H. Bourget, H. Buisson, and C. Fabry have continued their researches on the Orion Nebula. In a new paper presented to the Academy by M. Villard, the three savants deduce, from the interferential measures of radial speed and from the wave measures which they have accomplished, that the Nebula of Orion and the sun are going away from each other at the speed of 15·8 kilometres per second. The enormous gaseous mass of the nebula is not relatively at rest. It is thus that the North-East region is moving away at a speed of 5 kilometres per second, whereas that of the South-West is approaching at about the same speed. MM. Fabry, Buisson, and Bourget have applied their method to the identification of the rays of Nebulium with those of the terrestrial elements.

AN EXTREMELY RARE FISH.

Some Breton fishermen have just recently caught an extremely rare fish on the Brittany coast, near Qiberon. This fish was sold to an hotel and was eaten without any attention being given to it. However, an engineer noticed a certain number of exterior characteristics, and took some photographs of this unknown fish that fishermen call *Louvaron*, or white tunny. He sent a notice to M. Yves Delage, who consulted M. Jacques Pellerin, of the Natural History Museum. This latter recognised a *Luvius imperialis*, an exceptionally rare fish that lives in the middle Atlantic, in the waters of Madeira, where it is already very rare. It has also been found in the Straits of Gibraltar, in the Adriatic, and in the Mediterranean, but not farther than Crete. One single specimen had been taken at Concarneau a few years ago, another in the Ile of Ré in 1835; this fish is 1·15 m. long, with a diameter of 40 centimetres, and is from 20 to 25 centimetres wide. It has a smooth skin, red fins, and is exceedingly good to eat.

New Book.—Messrs. Crosby Lockwood and Son are announcing for publication in the autumn a new book on the "Chemistry of Petroleum and its Substitutes," by Drs. C. K. Tinkler and F. Challenger, of the University of Birmingham. The increasing importance of Petroleum has necessitated thorough scientific training of those concerned with the industry, and hitherto there has been no suitable book combining some technological matter with the purely theoretical and practical organic chemistry necessary to a comprehension of the methods employed. It will be remembered that the University of Birmingham has instituted a three years' course in Petroleum Mining.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 18, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President,
in the Chair.

THE PRESIDENT referred to the loss the Society had sustained, through death on June 6, 1914, of Prof. Dr. Adolf Lieben, who was elected an Honorary and Foreign Member on June 16, 1892.

Messrs. H. C. Reynard and R. L. Collett were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Frederick Raine Ennos, B.A., B.Sc., 98, Rectory Road, Stoke Newington, N.; Leon Maurice Hirschberg, Ph.D., 20, Birchington Road, Crouch End, N.; Benjamin Stanley Mellor, M.Sc., 42, Hill Crest View, Leeds; Olin Freeman Tower, Ph.D., Adelbert College, Cleveland, Ohio, U.S.A.; Arthur Henry Wardle, Ford House, Leek.

The following certificate has been authorised by the Council for presentation to ballot under By-law I. (3):—Ernest George, B.Sc., Victoria Square, King William's Town, S. Africa.

Messrs. F. P. Dunn and R. Gaunt were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared as duly elected:—Nicholas Alexander Auflogoff; Harry Berry; Alfred Archibald Boon, D.Sc.; Probodha Chandra Chattopadhyay, M.A.; Stanley Winter Collins, B.Sc.; Herbert William Cremer, B.Sc.; John Vernell Cutler; Shanazar Galstaun Galstaun, B.A.; James Mylam Gittins, M.Sc.; Frederick George Henderson; Victor Henri; Leonard Eric Hinkel, B.Sc.; Alfred Holt; John Cyril Jennings; John Orron Leighton; Robert Ernest Machin, B.Sc.; Ernest Ferguson Pollock, Ph.D.; Hashmat Rai, B.A., M.Sc.; Charles Edward Roberts, B.A., B.Sc.; Frederic Robinson, M.Sc.Tech.; Walter Edward Rowbottom; Thomas William Thompson, M.A.; Alfred John White, B.Sc.

Of the following papers, those marked * were read:—

*172. "Nitrogenous Constituents of Hops." By ALFRED CHASTON CHAPMAN.

In the case of a number of samples of hops analysed, the total percentage of nitrogen varied from 1·7 to 4 per cent, the percentages of soluble nitrogen varying from 0·44 to 0·9 per cent. The nitrogenous substances soluble in hot water consisted of soluble proteins, albumoses, ammonium salts, amino-compounds, and amides, bases precipitable by phosphotungstic acid, and unclassified nitrogenous substances not precipitated by that reagent. Results were given showing the proportions in which these various classes of compounds occur. In the course of the work, large quantities of hops and hop extract were worked with, and four distinct methods for the separation and isolation of the nitrogenous substances were employed. The following substances were isolated and identified:—L-Asparagine, aspartic acid, betaine, choline, histidine, hypoxanthine, and adenine. Of these asparagine and choline have been previously detected.

Two other bases were obtained, but in quantities too small to permit of their complete identification. One of these, however, was almost certainly arginine. Although considerable quantities of hops of various growths were employed, in no case was morphine, or any alkaloid closely resembling it, obtained. Potassium nitrate was present in appreciable quantities.

DISCUSSION.

Dr. POWER remarked, concerning the reference by Mr. Chapman to the alleged presence of morphine in hops, that no evidence had ever been adduced to justify the assumption that this alkaloid occurs in either wild or cultivated hops. The fact was recalled that about thirty

years ago a preparation was introduced under the name of "hopeine," which was first stated to have been obtained from "wild Virginian hops," and subsequently from "Arizona hops," but neither of these districts was known to produce hops in any amount. The so-called "hopeine" was examined by Ladenburg (*Ber.*, 1886, xix., 783), and others, who found it to consist of morphine or a mixture of the latter with a more readily soluble base. Dr. B. H. Paul (*Pharm. Journ.*, 1886, [iii.], xvi., 877) likewise showed it to be a variable product, consisting either chiefly of morphine or a mixture of morphine and cocaine, whilst in some samples the latter base predominated. The only presumption for the presence of morphine in hops appears thus to have been based on the statements concerning a product which was shown many years ago to have been of a purely fictitious character.

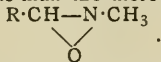
Mr. E. GRANT HOOPER inquired whether any investigation had been made of the solubility of the nitrogenous constituents of hops when a sugar or other carbohydrate solution was used instead of water. Considering that hops were chiefly used for brewing purposes, he thought that the solubility of the nitrogenous constituents in carbohydrate solutions was of some importance, and might be appreciably different from the solubility in water alone.

Mr. ROGERSON asked if the amount of betaine obtained by the lime method of extracting the hops was greater than the amount obtained by the other methods described. It was conceivable that some oxidation of choline might take place.

Mr. CHAPMAN said that he was aware of the episode to which Dr. Power had referred. So far as he knew, there was no evidence that certain kinds of wild hops did not contain small quantities of morphine or some similar alkaloid, but he thought it was quite clearly established that cultivated hops did not contain more than, at most, insignificant traces. Choline did not undergo conversion into betaine as readily as Mr. Rogerson seemed to imply, and having regard to the methods of extraction adopted in his (Mr. Chapman's) experiments, there could be no doubt that the betaine was actually present in the hops, and had not been formed from the choline during the process of examination. He had specially searched for the presence of tyrosine and guanine, but with negative results. He had, moreover, been unable to obtain any evidence of the presence of lysine.

*173. "The Isomerism of the Oximes. Part IV. The Constitution of the N-Methyl Ethers of the Aldoximes and the Absorption Spectra of Oximes, their Sodium Salts and Methyl Ethers." By OSCAR LISLE BRADY.

The author is of opinion that the constitution proposed by Angeli, Alessandri, and Aizzi-Mancini (*Atti R. Accad. Lincei*, 1911, [v.], xx., i., 546) for the N-methyl ethers of the oximes, namely, $R\cdot CH:N(CH_3):O$, is more in accordance with the facts than the more generally accepted isoxime structure,



The consideration of the absorption spectra of the oximes, their sodium salts, and their methyl ethers, obtained from benzaldehyde and *p*-nitrobenzaldehyde supports the views of Baly, Tuck, and Marsden (*Trans.*, 1910, xcvi., 571), that no trustworthy evidence can be obtained from spectroscopic considerations with regard to the structure of such compounds as the nitrophenols and their sodium salts.

*174. "The Wet Oxidation of Metals. Part III. The Corrosion of Lead." By BERTRAM LAMBERT and HERBERT EDWIN CULLIS.

Metallic lead, made by Stas's method, was fractionated by distilling in a quartz tube in a vacuum, and the middle fraction taken. This fraction was then distilled again, in a vacuum, in an apparatus so constructed that the distilled metal could be brought into contact with pure water and pure oxygen.

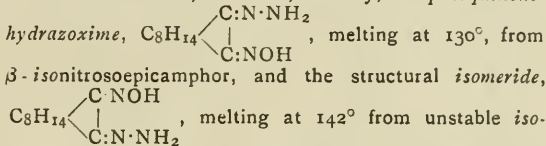
It was found that corrosion took place very rapidly if the oxygen was allowed to come into contact with the lead and water within a few days after the distillation of the lead.

If, however, the lead was left in contact with the pure water in a vacuum for twelve months, and then oxygen allowed to enter, the rate of corrosion was very slow. The metal retained a silvery-white appearance for more than a week, and even after six months the coating of oxide was so thin that it gave rise to interference colours.

The electrolytic theory of corrosion was considered in connection with lead.

*175. "Studies in the Camphane Series. Part XXXV. Isomeric Hydrazoximes of Camphorquinone, and some Derivatives of Aminocamphor." By MARTIN ONSLOW FORSTER and ERNEST KUNZ.

In order to investigate the possibility of stereoisomerism among hydrazoximes of camphorquinone, a systematic attempt was made to prepare the eight modifications required by theoretical considerations. Only two of these have been realised, however, namely, camphorquinone-



nitrosocamphor. Several derivatives of these compounds were described, together with various materials prepared from aminocamphor in the hope of obtaining the missing isomerides by indirect methods.

176. "The Velocities of Combination of Sodium Derivatives of Phenols with Olefine Oxides." By DAVID RUNCIMAN BOYD and ERNEST ROBERT MARLE.

The velocities with which ethylene and propylene oxides combine with sodium derivatives of phenols have been determined, approximately, for twenty-five phenols by estimating the yields of glycol aryl ethers produced when the olefine oxides are heated with N/20-alcoholic solutions of the phenolic salts.

The values found for $1/t \log 100/100 - x$ vary in the case of ethylene oxide from 0.34 for ψ -cumenol to 0.0073 for *o*-nitrophenol, and in the case of propylene oxide from 0.13 for ψ -cumenol to 0.0035 for *o*-nitrophenol. The following general conclusions are drawn:—

1. The reactivity of the sodium derivative towards ethylene oxide is increased by the presence of positive groups, for example, $\cdot CH_3$, $\cdot C_2H_5$, $\cdot CH_2\cdot CH:CH_2$, and diminished by the presence of negative groups, such as $\cdot O\cdot CH_3$, $\cdot CH:CH\cdot CH:CH\cdot$, $\cdot Cl$, $\cdot Br$, $C_6H_5\cdot N\cdot N\cdot$, $\cdot CN$, $\cdot NO_2$.

2. In general, the reactivity diminishes with increase in the acidity of the phenol. 2:4:6-Trichlorophenol, however, forms an exception to this rule, its sodium salt having a much higher reactivity than would be expected.

3. The phenols stand in almost the same order in the case of propylene as in the case of ethylene oxide. The most important exceptions are 2:4:6-trichloro- and 2:4:6-tribromo-phenol, α -naphthol, and *o*-chlorophenol. The sodium salts of these four phenols are much more reactive towards propylene oxide than would be anticipated from a consideration of the results obtained for the same phenols in the case of ethylene oxide.

4. There is no evidence of steric hindrance in the case of diortho-substituted phenols. The process of combination in the case of ethylene, and particularly in that of propylene oxide, seems rather to be facilitated by the presence of the two ortho-substituents.

Several new glycol aryl ethers were described.

177. "Colouring Matters contained as Glucoside in the Flowers of some Indian Plants." By ARTHUR GEORGE PERKIN and ISAAC SHULMAN.

These flowers, the description of which is given below, were specially collected in India, in the anticipation that

they contained some quantity of dyestuff. This has not proved to be the case, the amount of colouring matter isolated being extremely small, and, indeed, not always sufficient for analysis. The method of examination in each instance has consisted of treating the concentrated alcoholic extract with water, removal of suspended waxy matter, digestion of the aqueous solution with boiling hydrochloric acid to hydrolyse the glucosides, and isolation of the colouring matter by means of ether. Incidentally, the use of sodium hydrogen carbonate solution has been found of much service in purifying minute amounts of these substances. To this the crude product dissolved in alcohol is added, and, after agitation, ether now removes a fairly pure compound.

Poinciana regia (Bengal).—Three hundred and fifty grms. gave 0.31 gm. of colouring matter, which crystallised in yellow needles, dissolved in alkalis with a yellow coloration, and proved to be quercetin. The acetyl compound, colourless needles, m. p. 194–196°, gave C = 58.75; H = 3.84 per cent. An extract of these flowers had practically no dyeing action on mordanted cotton.

Impatiens balsamina (Chansili Pass) yielded but a trace of substance, evidently kaempferol. It separated from acetic acid in needles, m. p. 275–278°, and gave with sulphuric acid a fluorescent solution, whereas the acetyl derivative, colourless needles (found, C = 61.18; H = 4.06 per cent), fused at about 120°, re-solidified, and finally melted at 181–183°.

Woodfordia floribunda.—Seven hundred grms. gave 0.84 gm. of crude colouring matter, and this consisted of two substances readily separated by means of alcohol. The sparingly soluble compound (0.61 gm.) crystallised from pyridine in needles, and was recognised by analysis (found, C = 55.62; H = 2.40), the melting-point of the acetyl derivative (343–345°), and the Griessmayer reaction as ellagic acid. The soluble colouring matter (yellow needles, m. p. 285–291°), of which but a minute amount was available, was possibly an impure quercetin. It gave the general tests for this substance, but the acetyl compound, obtained in colourless needles, melted at 135–137°.

Erythrina stricta (vernacular name, "Konkathet"), from Chief Conservator of Forests (Mamyo, Burmah), gave a trace of kaempferol insufficient for analysis, which was recognised by the peculiar melting-point of the acetyl compound (see above), the fluorescence of its sulphuric acid solution, and its general properties.

For the samples of these flowers, the authors are indebted to Mr. D. Hooper, Reporter on Economic Products to the Government of India.

Mention may also be made here of the flowers of the common fuschia, *F. macrostema globosa*, which was found to yield traces of ellagic acid, identified by means of the acetyl compound (m. p. 343–345°), and quercetin, which gave acetylquercetin, m. p. 193–195°.

178. "Note on Quercitrin." By ARTHUR GEORGE PERKIN.

The statements (*Proc.* xxx., 151; *Trans.*, 1914, cv., 1411) that quercitrin has the formula $C_{21}H_{20}O_{11}$ and m. p. 183–185°, considered by the author at the time to be novel, are, in reality, not so, these facts having been previously ascertained by Brauns (*Arch. Pharm.*, 1904, cxlii., 561) and C. W. Moore (*Proc.*, 1910, xxvi., 182).

179. "A New Chlorocamphor." (Preliminary Note). By THOMAS MARTIN LOWRY and VICTOR STEELE.

By using the method described by Kipping in 1905 (*Proc.* xxi., 125), α -chlorocamphor has been converted into the stereoisomeric α' -chlorocamphor, which melts at 117°. A direct comparison gave the following values for the specific rotatory powers of the two compounds in alcoholic solution (5 grms. per 100 cc.):—

	Li 6708.	Na 5893.	Hg 5461.	Hg 4359.
α Chlorocamphor ..	70.0	97.0	119.2	242.9
α' -Chlorocamphor ..	27.5	41.4	54.1	140.9

180. "Ideal Refractivities of Gases." By WILLIAM JACOB JONES and JAMES RIDDICK PARTINGTON.

An equation has been deduced which permits of the correction of observed refractivities of gases at normal pressure, $P_0 = 760$ mm., and absolute temperature, $T_0 = 273.15$, for the deviations of the gases from the ideal state. This equation, which is based on D. Berthelot's characteristic equation, is:—

$$\mu' - 1 = (\mu - 1) \left[1 + \frac{9}{128} \pi (1 - 6r^2) \right]$$

where μ and μ' are the observed and ideal refractive indices respectively, $\pi = P_0/P_c$, $r = T_c/T_0$ (P_c and T_c are the critical constants). In the case of the permanent gases, the correction is inconsiderable, but it is appreciable in the case of the more easily liquefiable gases.

Gas.	Wave-length.	Refractive index at N.T.P.	Ideal refractive index.
Hydrogen	589	1.0001392	1.0001393
Methane	589	1.0004410	1.0004403
Xenon	486	1.0007130	1.0007078
Carbon dioxide ..	589	1.0004498	1.0004467
Sulphur dioxide ..	589	1.0006760	1.0006628
Chlorine	589	1.0007730	1.0007608
Cyanogen	436	1.0008710	1.0008536

181. " α -Bromonaphthalene: Its Physical Properties and its Application to the Determination of Water in Moist Alcohol." By MARIAN JONES and ARTHUR LAPWORTH.

The work referred to in a previous note on α -bromonaphthalene has been confirmed and extended (compare Crabtree and Lapworth, *Proc.*, 1912, xxviii., 264).

The temperatures at which homogeneous mixtures of α -bromonaphthalene and moist alcohol separate into two phases can be determined with exceptional readiness, and as these temperatures are very sensitive to alterations in the proportion of water present the authors use α -bromonaphthalene for ascertaining the composition of moist alcohol within the range, $H_2O = 1.45$ – 10.3 per cent. Data were quoted by means of which the percentage of water in small quantities of moist alcohol may be determined in a very simple manner, and with an error of less than 0.03 per cent.

182. "Colour and Constitution of Azo-compounds." Part VI. By JOHN THEODORE HEWITT, GLADYS RUBY MANN, and FRANK GEORGE POPE.

In previous communications attention has been drawn to the marked changes in colour which occur when solutions of paranitrated azophenols are rendered alkaline, and certain chemical evidence has been adduced in favour of the assumption that the salts possess a quinonoid structure.

Considering the possibility of enolisation taking place when an azo-compound contains a ketonic as well as a hydroxyl group, a number of azophenols have been prepared by diazotising p -aminoacetophenone and p -aminobenzophenone, and coupling them with phenol, p -cresol, and the naphthols. Alcoholic solutions of these compounds exhibit marked colour changes on addition of alkali.

183. "Studies in Phototropy and Thermotropy. Part IV. o -Nitrobenzylidenearylamines and their Photoisomeric Change." By ALFRED SENIER and ROSALIND CLARKE.

The authors have made a further search for examples of phototropy and thermotropy. The bases examined were o -nitrobenzylidenearylamines. All are thermotropic, and several exhibit phototropy. Prolonged exposure to light leads, however, to a non-reversible change in colour and in many cases to a change in melting-point. This change is ascribed to dimorphism. The interesting fact was discovered that these bases undergo photoisomeric change, like the compounds studied by Ciamician and Silber (*Ber.*, 1901, xxxiv., 2040), and that examined by Sachs and Kempf (*Ber.*, 1902, xxxv., 2704).

184. "Contributions to the Chemistry of the Terpenes. Part XVIII. Camphenanic Acid and its Isomerides."

By GEORGE GERALD HENDERSON and MAGGIE MILLEN
JEFFS SUTHERLAND.

The four isomeric acids of the formula $C_9H_{15}CO_2H$, which have been obtained by the oxidation both of camphene and of bornylene, were converted into their methyl esters; these are somewhat viscid, colourless liquids, which all boil at about the same temperature, 103–104°/22 mm. The esters of camphenilanic, *iso*-camphenilanic, and camphenanic acids yield the respective acids when hydrolysed, but the product obtained on hydrolysis of the supposed ester of *isocamphenanic* acid was found to be a mixture of camphenilanic and *iso*-camphenilanic acids. It is concluded that *isocamphenanic* acid is, in reality, a mixture of camphenilanic and *isocamphenilanic* acids, or else is converted into these acids during esterification.

Each of the esters, when treated with sodium and alcohol, yields the same alcohol, *camphenilanol*, $C_9H_{15}CH_2OH$, a crystalline solid melting at 77°, which is converted into campheninaldehyde by oxidation with chromic acid mixture. Its *hydrogen phthalate* crystallises in colourless plates, m. p. 153°, and its *p*-nitrobenzoate in yellow needles, m. p. 90°.

During the reduction of each of the esters, a small quantity of an acid was produced, and in every case this proved to be *isocamphenilanic* acid. Thus camphenilanic and camphenanic acids can be transformed into *isocamphenilanic* acid by a method different from those formerly described.

185. "2:3-Dibromonaphthalene." (Preliminary Note).
By WILLIAM PALMER WYNNE.

Different views have been held regarding the composition of the product obtained by dibrominating naphthalene: 1:4- and 1:5-dibromonaphthalenes have been isolated from it, but the nature of a third substance, m. p. 68° (*circa*), is still in doubt. Guareschi, who first recorded its presence in the dibromination product (*Gazzetta*, 1881, xi., 542), and Canzoneri, who obtained it by the interaction of phosphorus tribromide and bromo-*β*-naphthol (*Ibid.*, 1882, xii., 424), regard it as a single substance, but Armstrong and Rossiter consider it to be a definite compound of 1:4- and 1:5-dibromonaphthalene (*Proc.*, 1891, vii., 184). On the assumption that it is an individual, the only available structure is that of the 2:3-derivative, although this orientation is improbable on several grounds. For example, it would be the one exception to the rule that dibromonaphthalenes melt at temperatures higher than the corresponding dichloro derivatives, 2:3-dichloronaphthalene melting at 119.5°.

Through the kindness of the Badische Anilin- and Soda-Fabrik in supplying the author with 3-amino-*β*-naphthoic acid, an opportunity has arisen for the preparation of 2:3-dibromonaphthalene, hitherto unknown. The following compounds were described:—3-bromo-*β*-naphthoic acid, $C_{10}H_6BrCO_2H$, needles, m. p. 220°; the methyl ester, needles, m. p. 67°; the hydrazide, minute needles, m. p. 218°; the urethane, needles, m. p. 114°; 3-bromo-2-naphthylamine, $C_{10}H_6BrNH_2$, scales, m. p., 168°, and its acetyl derivatives, clusters of scales, m. p. 172°. 2:3-Dibromonaphthalene, which forms silvery, rectangular scales, m. p. 140, has the same melting-point as recorded for the 2:7-derivative by Jolin (*Bull. Soc. Chim.*, 1877, [ii.], xxviii., 514), but as the method used by him is open to criticism, the preparation of the 2:7-compound is being undertaken for the purpose of comparison by reactions which avoid the use of phosphorus pentabromide at high temperatures.

186. "Calcium Nitrate. Part III. The Three-component System: Calcium Nitrate—Lime—Water." By HENRY BASSETT, jun., and HUGH STOTT TAYLOR.

The conditions of equilibrium in this system have been studied at 25° and at 100°.

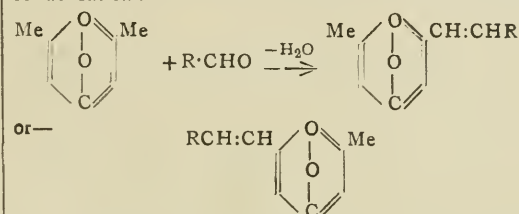
The compounds capable of existing in equilibrium with solution at 25° are:— $Ca(OH)_2$, $Ca_2N_2O_7 \cdot 3H_2O$, and $Ca(NO_3)_{2.4}H_2O$; whilst at 100° they are:— $Ca(OH)_2$,

$Ca_2N_2O_7 \cdot 2H_2O$, $Ca_2N_2O_7 \cdot \frac{1}{2}H_2O$, and $Ca(NO_3)_2$. The series of solid solution CaO, xN_2O_5, yH_2O , which according to Cameron and Robinson (*Journ. Phys. Chem.*, 1907, xi., 273) exists at 25°, has not been confirmed. It has, on the contrary, been shown that the region of solid solutions described by these authors is really a portion of the region where $Ca(OH)_2$ is the stable solid phase.

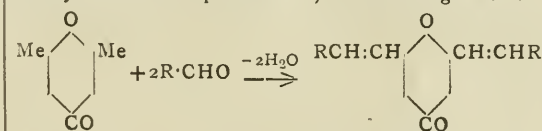
It was suggested that the presence of a trace of magnesia in the calcium nitrate used by Cameron and Robinson may have led them to erroneous conclusions.

187. "Some Arylidenedimethylpyrones and their Salts." By ALFRED ARCHIBALD BOON, KENNETH JOHN MCKENZIE, and JOHN TROTTER.

Not long after Collie suggested the bridged formula for dimethylpyrone (*Trans.*, 1904, lxxxv., 973), one of the authors was induced to study the action of furfuraldehyde on this base with the view of effecting the following condensation:—



For this purpose many experiments were undertaken under varying conditions, but in every case both the methyl groups of dimethylpyrones took part in the reaction. More recently (*Proc.*, 1910, xxvi., 95) it was indicated that the condensation of dimethylpyrone with an aldehyde could be represented by the following scheme:—



and that the resulting coloured base formed intensely coloured salts with acids, the colour of the salts depending on the nature of the aldehyde used in condensation as well as that of the acids employed in their production. Attention is now called to three of these bases, namely, *bisfurylidenedimethylpyrone*, *bisbenzylidenedimethylpyrone*, and *bisanisylidenedimethylpyrone*, and some of their salts. All these salts undergo hydrolysis when boiled with water.

In a subsequent paper the constitution of the various compounds indicated here will be discussed by one of the authors with other collaborators.

Each of the bases just mentioned was prepared by the action of the aldehyde on dimethylpyrone in the presence of alcoholic sodium hydroxide. *Bisfurylidenedimethylpyrone*, $C_{17}H_{12}O_4$, is yellow, and melts at 200°. Each of the following salts, which are red, was obtained in the following way:—A 20 per cent solution of the acid was allowed to act on the base dissolved in an alcohol, in the case of the hydrochloride amyl alcohol being used, and for the other salts methyl alcohol. Each salt was washed with light petroleum, and dried in a vacuum.

The hydrochloride, $C_{17}H_{12}O_4 \cdot HCl$, m. p. 196° (becoming yellow at about 115°).

Found— $HCl = 11.29$. Calc., $HCl = 11.50$ per cent.

The nitrate, $C_{17}H_{12}O_4 \cdot HNO_3$, m. p. 166–167° (changes colour at 102°).

Found— $HNO_3 = 18.02$. Calc., $HNO_3 = 18.38$ per cent.

The sulphate, $C_{17}H_{12}O_4 \cdot H_2SO_4$, m. p. 202–203°.

Found— $H_2SO_4 = 24.70$. Calc., $H_2SO_4 = 25.92$ per cent.

Bisbenzylidenedimethylpyrone, $C_{21}H_{16}O_2$, forms faintly yellow crystalline flakes, melting at 168°. The following yellow salts were isolated, and in the preparation of each of them the respective acids were allowed to act on the base dissolved in chloroform.

For the nitrate a 20 per cent solution of nitric acid was used, and for the hydrochloride and the sulphate, acids having respectively D 1.11 and D 1.32 were employed.

The hydrochloride, $C_{21}H_{16}O_2 \cdot HCl$, m. p. $166-167^\circ$.

Found— $HCl = 10.65$. Calc., $HCl = 10.85$ per cent.

The nitrate, $C_{21}H_{16}O_2 \cdot HNO_3$, m. p. $141-142^\circ$ (with decomposition).

Found— $HNO_3 = 16.98$. Calc., $HNO_3 = 17.38$ per cent.

The sulphate, $C_{21}H_{16}O_2 \cdot H_2SO_4$, m. p. $155-156^\circ$, darkens about 104° .

Found— $H_2SO_4 = 25.80$. Calc., $H_2SO_4 = 24.68$ per cent.

Bisauisylidenedimethylpyrone, $C_{23}H_{20}O_4$, forms faintly yellow crystalline flakes melting at 199° . With the exception of the deliquescent, bright red sulphate, the inorganic and organic salts prepared from this base lose weight when exposed to the air, during periods varying from eleven to thirty days, the nitrate being most stable, the formate losing all its acid, and the hydriodide becoming dark violet.

Inorganic Salts.—The hydrofluoride is yellow, but all the other salts are red. Unless otherwise stated, each salt was prepared by allowing an excess of the concentrated acid dissolved in alcohol to act on a boiling alcoholic solution containing 2 grms. of the base. In some cases the freshly prepared salt was dried and immediately analysed (for example, the bright red sulphate), whilst in other cases it was either washed with alcohol (for example, the nitrate) or recrystallised from methyl alcohol (for example, the hydrochloride) before being dried and analysed.

The hydrochloride, $C_{23}H_{20}O_4 \cdot HCl$, m. p. $147-148^\circ$.

Found— $HCl = 8.89$. Calc., $HCl = 9.20$ per cent.

The hydrobromide, $C_{23}H_{20}O_4 \cdot HBr$ (m. p. not sharp).

Found— $HBr = 18.08$. Calc., $HBr = 18.36$ per cent.

The hydrofluoride, $C_{23}H_{20}O_4 \cdot HF$, decomposes when heated. In its preparation at least four times the calculated quantity of acid must be used. The salt when freshly prepared is red, but on drying in a vacuum over sodium hydroxide until its weight is constant it becomes yellow.

Found— $HF = 5.23$. Calc., $HF = 5.26$ per cent.

(From various experiments the action of hydrofluoric acid on the base appears to be abnormal).

The nitrate, $C_{23}H_{20}O_4 \cdot HNO_3$, decomposes at 146° .

Found— $HNO_3 = 14.78$. Calc., $HNO_3 = 14.89$ per cent.

The sulphate, $(C_{23}H_{20}O_4)_2 \cdot H_2SO_4$, forms dark red crystals, m. p. $86-87^\circ$. The calculated quantity of concentrated sulphuric acid mixed with 10 cc. of alcohol was used in its preparation.

Found— $H_2SO_4 = 12.25$. Calc., $H_2SO_4 = 11.98$ per cent.

The sulphate, $C_{23}H_{20}O_4 \cdot H_2SO_4$, bright red crystals, m. p. 101° . To a solution containing 50 cc. of alcohol and 20 cc. of concentrated sulphuric acid 2 grms. of the base were added, and the mixture was heated for half-an-hour on a water-bath.

Found— $H_2SO_4 = 21.42$. Calc., $H_2SO_4 = 21.39$ per cent.

The platinichloride, $(C_{23}H_{20}O_4)_2 \cdot H_2PtCl_6$.—A slight excess of a concentrated alcoholic solution of platinic chloride was added to a boiling alcoholic mixture containing the base and excess of concentrated hydrochloric acid.

Found— $Pt = 17.11$. Calc., $Pt = 17.25$ per cent.

Organic Salts.—These are mostly yellow compounds, but a formate, a tartrate, and the picrate are red, whilst the salicylate is yellowish red.

The formate, $C_{23}H_{20}O_4 \cdot (CH_2O)_2$, is a red salt, m. p. 99° , unstable when exposed to the air, becoming yellow, and finally losing all its acid. It is prepared by heating a solution of the base in pure formic acid on a water-bath, then allowing the solution to remain at the ordinary temperature, washing the salt with 50 per cent formic acid, drying, and immediately analysing.

Found— $CH_2O_2 = 19.62$. Calc., $CH_2O_2 = 20.35$ per cent.

The formate, $C_{23}H_{20}O_4 \cdot CH_2O_2$, consists of yellow hair-like crystals, and suffers decomposition when heated. It is obtained by the action of 90 per cent formic acid on the base.

Found— $CH_2O_2 = 11.20$. Calc., $CH_2O_2 = 11.33$ per cent.

The acetate, $C_{23}H_{20}O_4 \cdot C_2H_4O_2$, forms yellow hair-like crystals, and is obtained by gently warming a solution of the base in 90 per cent acetic acid, and allowing the mixture to remain at the ordinary temperature. The crystals were washed with 50 per cent acetic acid, dried, and immediately analysed.

Found— $C_2H_4O_2 = 14.44$. Calc., $C_2H_4O_2 = 14.30$ per cent.

The oxalate, $(C_{23}H_{20}O_4)_2 \cdot C_2H_2O_4$, which forms yellow needles, was obtained by adding a slight excess of the calculated quantity of anhydrous oxalic acid to a solution of the base dissolved in toluene (some alcohol being added to keep the base in solution). The mixture was boiled for six hours on the water-bath, and then allowed to cool at the ordinary temperature.

Found— $C_2H_2O_4 = 11.75$. Calc., $C_2H_2O_4 = 11.11$ per cent.

The oxalate, $C_{23}H_{20}O_4 \cdot C_2H_2O_4$, which separates in yellow crystals, m. p. $174-175^\circ$, was prepared by gradually adding 1 gm. of anhydrous oxalic acid to a boiling toluene solution of 2 grms. of the base. The solution was allowed to remain at the ordinary temperature after being boiled for six hours.

Found— $C_2H_2O_4 = 19.62$. Calc., $C_2H_2O_4 = 20.00$ per cent.

The tartrate, $(C_{23}H_{20}O_4)_2 \cdot C_4H_6O_6$, forms red crystals, and was obtained in a manner similar to that employed for the preparation of the corresponding oxalate.

Found— $C_4H_6O_6 = 17.45$. Calc., $C_4H_6O_6 = 17.24$ per cent.

The succinate, $(C_{23}H_{20}O_4)_2 \cdot C_4H_6O_4$, is yellow, and the salicylate, $(C_{23}H_{20}O_4)_2 \cdot C_7H_6O_3$, yellowish red. These were obtained by heating the base for a number of hours with a concentrated alcoholic solution of the respective acids. In the case of the salicylate, the alcohol contained about 5 per cent of toluene.

Found— $C_4H_6O_4 = 14.65$. Calc., $C_4H_6O_4 = 14.42$ per cent.

Found— $C_7H_6N_3 = 28.57$. Calc., $C_7H_6O_3 = 27.71$ per cent.

The picrate, $C_{23}H_{20}O_4 \cdot C_6H_3O_7N_3$, prepared by adding an alcoholic solution of picric acid to a boiling alcoholic solution of the base, forms red needles, m. p. 211° .

Found— $N = 7.62$. Calc., $N = 7.13$ per cent.

(To be continued).

MISCELLANEOUS.

Institute of Chemistry.—The Council will be prepared to arrange examinations in Chemical Technology to be held in October, 1914. The examinations will be open only to Fellows, and to those Associates who have been registered as such for at least one year, who produce evidence of practical technological training. An Examination in Biological Chemistry, Bacteriology, Fermentation, and Enzyme Action will commence on Monday, October 19, 1914. The Examination will be open to Fellows and Associates, to candidates whose applications for admission to the Final Examination have been accepted by the Council, and to candidates who have passed the Intermediate Examination of the Institute, provided in each case that they produce evidence, satisfactory to the Council, of having taken a course in Elementary Biology, as defined in the Regulations. The Examination extends over five days, and may be theoretical and practical, and both written and oral. The syllabus includes Biological Chemistry, Bacteriology, Fermentation, and Enzyme Action, with special reference to the Chemistry and Bacteriology of Food-Stuffs, Water Supply, and Sewage Disposal, and the application of Biological Chemistry to Industries and Manufactures. Fellows and Associates who desire to present themselves are required to send in their applications not later than Tuesday, September 15, 1914. Forms of application and full particulars can be obtained from The Registrar, Institute of Chemistry, 30, Bloomsbury Square, London, W.C.

THE CHEMICAL NEWS.

VOL. CX., No. 2855.

ON THE CALCULATION OF CONSTANTS FOR THE HEATS OF COMBUSTION OF HYDROCARBONS.

By H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S.

IN THE CHEMICAL NEWS (vol. cx., pp. 26 and 37) Mr. Gervaise Le Bas has resuscitated a method for calculating constants for the heats of combustion of hydrocarbons, concerning which I supposed that the last word had been said by myself seven years ago (CHEMICAL NEWS, 1907, xcvi., 136). I do not wish unnecessarily to repeat criticisms then made; moreover, Mr. Le Bas, no doubt profiting by my former criticisms, has, on the present occasion, more carefully worded his statements, so that not all these criticisms now stand. There is much, however, in his new contribution that calls for critical comment.

Mr. Le Bas says that "the observed heats of combustion . . . are . . . likely to be additive . . ." The word "additive" is not free from ambiguity. In one sense it means that the property in question of a compound is the sum of the properties of its elements. Thus, the molecular weight of a compound is the sum of the atomic weights of its elements. In this sense heat of combustion is certainly not an additive property. But instead of allocating a property to the elements it may be allocated to the valency linkages between them, and in the sense thus derived it is not merely likely that heat of combustion is an additive property, but I have conclusively proved that such is the case within the limits of experimental error, and apart from a very few exceptional cases. The absolute necessity of allocating the constants to the valency-linkages and not merely to the atoms, is evident from the fact that if constants are calculated on the latter hypothesis new values have to be assigned, or corrections introduced, for every change of linkage. Thus, Mr. Le Bas calculates certain constants from saturated hydrocarbons, which he terms the effective heat of combustion values of C and H, namely, $C = 106.0$ cal., $H = 26.48$ cal. But if one wishes to use these for compounds containing linkages other than those present in saturated hydrocarbons (e.g., unsaturated hydrocarbons), corrections for the new forms of linkage must be introduced. It is possible, however, to reverse the process. One could calculate the effective heat of combustion values of C and H for a body like ethylene, containing only C:C and C:H linkages, and introduce a correction for the C:C linkage. The values, to be precise, are $C = 121.8$ cal., $H = 22.25$ cal., correction for C:C = -8.0 cal. This gives:—

Compound.	M.H.C. (Thomsen, const. vol.)	M.H.C. (calculated).
	Cals.	Cals.
Ethylene, $CH_2:CH_2$	332.2	332.6
Propylene, $CH_3:CH:CH_2$. .	491.3	490.9
iso-Butylene, $C_2H_5:CH:CH_2$.	648.9	649.2
Diallyl, $CH_2:CH:(CH_2)_2CH:CH_2$	930.8	929.3

In a similar manner, effective heat of combustion values for C and H could be calculated for any type of compound. In view of the possible multiplicity of such values the method seems highly arbitrary and cumbersome, and compares very badly with my own method of calculating thermo-chemical constants developed in several papers published in vols. xcv., xcvi., xcvi., and xcvi. of the CHEMICAL NEWS (published in book-form, after revision, by Mr. Edward Arnold, in 1909, under the title of "On the Calculation of Thermo-chemical Constants"), in which all the constants used have precise definitions

attached to them. Moreover, these "effective values" of the elements can readily be obtained from my own constants. Those of Mr. Le Bas, for instance, are $C = \alpha - 2\beta$, $H = \frac{\beta}{2}$, correction for C:C = $2\beta - \gamma$ (as I shall show later), whereas the ones I have just used for ethene hydrocarbons are $C = \alpha - \gamma$, $H = \frac{\gamma}{4}$, correction

for C:C = $\frac{\gamma}{2} - \beta$, where α , β , and γ are my constants as in the work referred to.

I have proved that every hydrocarbon must conform to the formula—

$$nC + 2(n+1 - \alpha - 2\beta - \rho)H + (n + \rho - \alpha - \beta - 1)L_1 + \alpha L_2 + \beta L_3$$

where every H atom is accompanied by a C:H linkage, and L_1 , L_2 , L_3 stand respectively for a C.C., a C.C., and a C:C linkage. n , α , β , and ρ are, of course, whole numbers, whose values depend upon the constitution of the hydrocarbon. This formula may also stand for the heat of combustion of the hydrocarbon, where C is the amount due to a free C atom, H that due to a H atom bound to C, and L_1 , L_2 , L_3 are the respective effects of these linkages. It is necessary, however, as I have shown, to add on a certain value, say, T, in the case of a body whose valencies are strained, other than in the formation of C:C or C:C linkages (e.g., trimethylene).

As I have proved, the values of C, H, L_1 , L_2 , and L_3 are indeterminate at the present stage of knowledge. It is possible, however, to calculate the heats of combustion of hydrocarbons (and other bodies) by means of suitably chosen derived constants. My own "fundamental constants" are $\alpha = C + 4H$, $\beta = 2H - L_1$, $\gamma = 4H - L_2$, $\delta = 6H - L_3$, which give the equation—

$$nC + 2(n+1 - \alpha - 2\beta - \rho)H + (n + \rho - \alpha - \beta - 1)L_1 + \alpha L_2 + \beta L_3 + T = n\alpha - (n + \rho - \alpha - \beta - 1)\beta - \alpha\gamma - \beta\delta + T.$$

Now, as I have shown, the thermic values of the intramolecular strains in a C:C and a C:C link, T_2 and T_3 , are given respectively by the equations, $T_2 = L_2 - 2L_1 = 2\beta - \gamma$, and $T_3 = L_3 - 3L_1 = 3\delta - \delta$.

Substituting these values in the above equation we get—

$$nC + 2(n+1 - \alpha - 2\beta - \rho)H + (n + \rho - \alpha - \beta - 1)L_1 + \alpha L_2 + \beta L_3 + T = n\alpha - (n + \rho + \alpha + 2\beta - 1)\beta + \alpha T_2 + \beta T_3 + T,$$

Now, put $X = \alpha - 2\beta$, $Y = \frac{\beta}{2}$; the above equation then

reduces to—

$$nX + 2(n+1 - \alpha - 2\beta - \rho)X + \alpha T_2 + \beta T_3 + T;$$

and comparing this equation with that of the general hydrocarbon it will be seen that coefficient of X = coefficient of C, coefficient of Y = coefficient of H, coefficient of T_2 = coefficient of L_2 , and coefficient of T_3 = coefficient of L_3 . It is evident, therefore, that X and Y are Mr. Le Bas's effective values of C and H (provided these have been calculated correctly), and that T_2 and T_3 are his C:C and C:C corrections respectively. It follows that nothing which can be shown by his method concerning the constitution of the hydrocarbons has not been or could not be shown by my method. As a matter of fact, Mr. Le Bas's remarks about cyclic hydrocarbons and benzene are all stale. I showed in the book already mentioned how the thermochemistry of organic compounds entirely substantiates von Baeyer's strain theory, calculating and graphing the thermic values per linkage of the strain in the C:C and C:C bonds, and in carbon rings containing 3 to 6 members, as well as that in ethylene oxide. And I have pointed out that the heat of combustion of benzene conclusively shows the inadmissibility of Kekulé's formula, the thermic value of the intramolecular strain in that body being less than that due to one C:C linkage.

Before dealing further with the question of the constitution of benzene it is necessary to insist on the fact that Mr. Le Bas's constants have not been calculated with entire accuracy. He finds that the heats of combustion

of the simple paraffins are in the ratio 8 : 14 : 20 . . . &c., these numbers being the valency numbers (sum of valencies holding the compound together) of these bodies. He adds that that "the constant [M.H.C. ÷ valency number (n)] is obviously the combustion value of (H) under the circumstances." The word "obviously" seems to be introduced merely as an excuse for giving no reason for this assumption. In order that it shall be true, it is necessary that $X=4Y$; i.e., that $\alpha-2\beta=2\beta$, i.e., that $\alpha=4\beta$.

In the first place the accuracy of Mr. Le Bas's calculations are vitiated by his omission to correct for constant volume. If this is done, and the values of α and β calculated by means of the theorem of least squares from the five simplest paraffins investigated by Thomsen, we get $\alpha=210.7$ cal., $\beta=52.4$ cal. If, as I have done, we allow superior accuracy to the value for methane (an assumption justified on the ground that the size of the probable error depends upon the size of the quantity measured) we get $\alpha=210.8$ cal., $\beta=52.5$ cal. In neither case is $\alpha=4\beta$ accurately. It is evident, therefore, that Mr. Le Bas has not discovered any law between heat of combustion and valency number, but has merely hit upon an accidental relationship, namely, $\alpha=4\beta$ approximately. If any "law" were involved, it would hold for compounds containing other elements (e.g., the halogens, oxygen, sulphur, nitrogen, &c.), which is not, in fact, the case.

It should be noticed that the above figures give $X=105.9$ or 105.8 , $Y=26.2$ or 26.25 , whereas Mr. Le Bas gives $X=106.0$, $Y=26.48$, in that part of his paper dealing with chain hydrocarbons. When, however, we turn to his alleged explanation of the thermic behaviour of benzene and its reduction-products we find him using $X(=4Y)=104.0$, $Y=26.0$! Moreover, in the first case the correction for the C : C linkage (T_2) is given as 15.8 ; in the latter as 8.0 ! Evidently we are not here in the region of explanation.

My own "fundamental constants," calculated from Thomsen's data, give the following results for the differences between the M.H.C.'s of benzene and its reduction products:—

Hydrocarbon.	Formulae.	Formulae of Δ .	Cals.
Benzene	C_6H_6	$6\alpha-9\beta$	
Dihydrobenzene ..	C_6H_8	$6\alpha-4\beta-2\gamma$	$5\beta-2\gamma$
Tetrahydrobenzene	C_6H_{10}	$6\alpha-5\beta-\gamma$	$-\beta+\gamma$
Hexahydrobenzene	C_6H_{12}	$6\alpha-6\beta$	$-\beta+\gamma$
Hexane	C_6H_{14}	$6\alpha-5\beta$	$+\beta$

These values do not agree well with those found experimentally by Stohmann, but this is what we should expect from the facts—(i.) that Thomsen and Stohmann carried out their experiments by different methods and under different conditions (Thomsen gives 797.9 cal. for benzene at const. vol.), and (ii.) that the formation of the benzene ring is accompanied by a certain amount of strain, equivalent, according to Thomsen's figures, to 5.6 cal. But it should be noticed that there is an agreement in the order of magnitude of these differences. The difference between benzene and dihydrobenzene is greatest, whilst those between dihydrobenzene, tetrahydrobenzene, and hexahydrobenzene are equal and least.

If these differences are calculated by means of Mr. Le Bas's original constants (i.e., those given in part one of his paper), similar values are obtained, namely, 84.6, 37.2, 37.2, and 53.0 cal. respectively, which was to be expected from the fact that these constants can be obtained from mine.

Finally, as concerns the constitution of benzene: as I have already stated, I agree with Mr. Le Bas in rejecting Kekulé's formula. I also agree with him in rejecting the dynamical formulæ of Collie, Baly, and others, for the different phases of such formulæ represent different amounts of energy; hence a recurrent and spontaneous transformation through a series of such phases would be contrary to the second law of thermodynamics, and

would, in any case, be accompanied by changes in the temperature of the body.

Nor will the singly-linked, saturated types of formulæ, such as those of Claus, Ladenburg, and Thomsen, satisfy the conditions; for such formulæ postulate the existence in the benzene-molecule of three and four-membered carbon rings, which rings can only exist in a state of tension, and are accompanied by considerable increments in the heats of combustion.

I think a good deal may be said for Thiele's formula, though I generally use Armstrong's and Baeyer's as being less definite, and, therefore, less hypothetical. We know that when a force is constrained to perform work along some direction other than that in which it acts, part of it alone is effective, that called the component in that direction. It may be possible to explain intramolecular strain as due to that component of the valency which is not active in binding the atoms together. Thiele's formula for benzene assumes that these components mutually satisfy one another. There are difficulties in the geometrical treatment of this supposition, however, as well as when we attempt to deal mathematically with the thermic values of the strain per linkage in unsaturated and ring compounds, which values should, on this hypothesis, be proportional to the sines of the angles of deviation; but unfortunately, so far as can be determined from the data at hand, are not. Nothing really definite can be said, however, until further information concerning the thermic behaviour in the gaseous state of compounds containing three, four, five and more carbon atoms is available. This should prove a rich field of research for anyone with the requisite ability and means, and much light might thereby be thrown on the puzzling problem of the nature of valency.

SYNTHETIC RESINS.*

By L. V. REDMAN, A. J. WEITH, and F. P. BROCK.

(Continued from p. 67).

THE ANHYDROUS REACTION BETWEEN HEXAMETHYLENE-TETRAMINE AND PHENOL.

Hexamethylenetetramine Triphenol.

THE simplest product which forms when phenol reacts with hexamethylenetetramine is the addition product hexamethylenetetraminetriphenol which crystallises out of a cold water solution (Moschatos and Tollens, *Ann. der Chemie*, ccii., 280).

Lebach (*Zeit. f. Angew. Chemie*, 22nd year, 1600—1909), 1909, states that hexamethylenetetramine triphenol when heated by itself, i.e., in the dry, goes over with the evolution of ammonia into "einen gelben unlöslichen und unschmelzbaren Körper über, der nichts anderes ist als Bakelit." The reason for this conclusion doubtless lies in the fact that the insoluble material has the same yellow, transparent, glossy appearance as Bakelite which has been made from phenol and formaldehyde using ammonia as the condensing agent. However this may be, the material has not at all the same composition as Bakelite. Dr. Bakeland gives as his conclusion from his experiments that Bakelite consists of a material in which 6 phenols have united with 7 methylene groups (*Journ. Ind. and Eng. Chem.*, i., March, 1909; v., June, 1913).

Hexamethylenetetraminetriphenol has a composition of 6 phenols for every 12 methylenes, or 41.7 per cent more methylene than is necessary for making Bakelite.

Another argument which must be brought in opposition to this conclusion, lies in the fact that Dr. Bakeland represents the addition of the seventh formaldehyde group directly to the molecule without the elimination of the oxygen in the formaldehyde as shown in the equation

* *Journal of Industrial and Engineering Chemistry*, vi., No. 1.

(see *prox.*) with the elimination of water. Now in the dry this final reaction cannot possibly take place. No oxygen or water is present to form with the methylene group, formaldehyde. Indeed the only oxygen present in the reaction is contained in the hydroxyl of the phenol, and as we show in the case of anisol and phenetol (see *prox.*) when the hydroxyl group becomes inactive no reaction takes place between hexamethylenetetramine and the compound containing the benzene nucleus, it seems reasonable, therefore, to assume that the oxygen of the hydroxyl is not interfered with as this reaction proceeds normally and produces the insoluble resin. We show elsewhere (see *prox.*) that in the reaction between phenol and hexamethylenetetramine no water is evolved.

When hexamethylenetetraminetriphenol is heated, there escapes not only ammonia and a small amount of phenol, but also there is present a strong fishlike or mouse odour of methylamines. The latter by-product is not present when the phenol is increased to 6 mols. of phenol to 7 methylenes. Such a resin with twice the amount of necessary methylene would be not only costly but useless both in the quality of the resin and the offensive methylamine odour which it possesses.

With the formation of different by-products, the absence of water or oxygen to form methyleneglycol or formaldehyde, thereby preventing the hardening process from taking place according to Dr. Baekeland's formula, and the proportions of phenol to methylenes being 6:12 instead of 6:7, it seems untenable to hold that the yellow material which forms when hexamethylenetetramine triphenol is heated in the dry is Bakelite.

The resin aggregate resulting from the heating of dry hexamethylenetetramine triphenol at 175° C. or higher for one hour, with the evolution of ammonia and methylamines, will swell, soften, and partly dissolve or disintegrate in boiling phenol with a strong evolution of ammonia. This indicates the very evident fact that hexamethylenetetramine or some of its degradation products are present in some form in the resin. A further proof of this lies in the fact that the aggregate swells in dilute HCl. No other resin which we have made swells in acid. All other resins, even the alcohol-soluble "Novolak," remains quite unaffected in an acid solution. The swelling indicates that there is present in the aggregate a material which is soluble in acid.

In the wet process it is impossible to say that the substance which is reacting in solution to produce the resin is hexamethylenetetramine triphenol. There are no methylamines given off as by-products and the excess hexamethylenetetramine remains in the water solution, while the resin which forms has a ratio of phenol to methylene 13:12 in the early stages of heating and the final product has a ratio of 6:6.

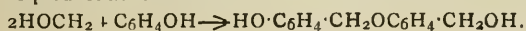
Hexamethylenetetramine and Phenol (Wet Process).

When 1 mol. of hexamethylenetetramine and 6 mols. of phenol are dissolved in 500 cc. of water and the solution boiled, a light yellow coloured, transparent, amber-like viscous liquid begins to separate out which on continued heating becomes very viscous and finally changes to a brittle amber solid when cold. This reaction is probably identical with that which takes place when 1 mol. of formaldehyde and 1 mol. of phenol are heated together, using ammonia as a condensing agent to hasten the reaction.

The general conditions have been presented which occur when an active methylene group reacts with a phenolic body in the presence of water. A very different set of reactions takes place when no water is present during the reaction.

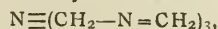
By-products of the Dry Reaction.

When formaldehyde is used the by-product formed is water, the reaction taking place with the dehydration of the product as follows:—

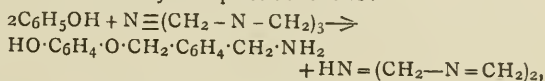


The reaction continues with increasing size of the molecule and further elimination of water.

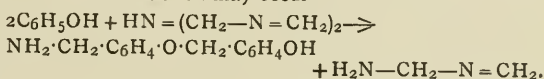
If, however, dry hexamethylenetetramine and anhydrous phenol be mixed together and the mixture heated at 60° C. or higher a reaction begins with the evolution of ammonia, and ammonia is the only by-product, as shall be shown later. If the phenol be present in excess, and if the mass be heated to the boiling-point, the reaction is very rapid. Practically all the ammonia is given off in the first ten minutes of the boiling, and the reaction is quite complete and all the nitrogen has been evolved as ammonia within two hours from the beginning of the reaction. The reaction takes place probably in a series of steps. Accepting the formula of hexamethylenetetramine as—



this reaction may take place as follows:—



and a second reaction may occur—



This process continues until all the CH₂ groups have combined with the phenol and ammonia remains as the by-product. The intermediate product, aminosalignenol, has been isolated and will be described in a later paper. No nitrogen and no methylamines are given off in measurable quantities at any stage in the process. No water is formed (Baekeland, *Journ. Indust. and Eng. Chem.*, 1911, iii., 932; 1912, iv., 741) and the nitrogen contained in the hexamethylenetetramine is evolved quantitatively as ammonia as will be shown later (see *prox.*). This reaction between a phenolic body and an active methylene group may be followed by simply measuring the amount of ammonia which has been evolved. This is especially true if the phenol is in excess, e.g., if 24 mols. of phenol be heated with 2 mols. of hexamethylenetetramine the final product is a resin in which the methylene groups have united with the phenols in the ratio of 13 phenols to 12 methylenes (see *prox.*). The remaining 11 mols. of phenols are present as free phenol and may be separated easily from the resin by dissolving the mass in dilute sodium hydroxide after the ammonia has all been evolved, neutralising the solution or making it acid with HCl and filtering off the precipitated resin.

THE RESINS IN EXCESS PHENOL.

The resin which forms when hexamethylenetetramine is heated in the presence of excess anhydrous phenol seems always to be the same material and resembles very closely Novolak (see analysis of Novolak, *prox.*). It is soluble in alcohol, acetone, phenol, caustic, &c., and is insoluble and precipitated from its solution by acids. Heated, it does not harden rapidly but remains a liquid at high temperatures, melting at 105–110° C. and remaining liquid at 180° C. for many hours. If the heating is continued, a flexible dark red skin forms over the surface which is only partly soluble in alcohol. A peculiar gas is given off during the heating which has the odour of burning phenol. When cold the resin hardens to a glossy material which is more brittle than common resin and apparently quite useless as a commercial product. This resin is not a solution of the final product in phenol but is an individual having definite chemical properties and heating does not readily polymerise it.

A variation in the amount of excess phenol present does not alter the characteristics or the amount of the synthetic resins formed when a definite amount of hexamethylenetetramine is used; e.g., if 18 mols. of phenol and 1 mol. of hexamethylenetetramine be heated until the ammonia has ceased to evolve, the same amount of resin is formed

and the resin has the same characteristics as when 12 mols. of phenol are heated with 1 mol. of hexamethylenetetramine until ammonia ceases to evolve.

As the amount of excess phenol is gradually decreased the mass which is left in the flask after the ammonia has ceased to come off changes its physical properties, for all combinations of phenol with hexamethylenetetramine; those above 12 mols. of phenol to 1 mol. of hexamethylenetetramine remain a yellow liquid whether hot or cold, and are in reality a solution composed of the soluble resin described above and the unused phenol. But as the phenol is decreased below the ratio of 12 mols. of phenol to 1 mol. of hexamethylenetetramine, the liquid thickens and finally, as the excess of free phenol decreases, the resin changes to an infusible insoluble transparent yellow or red solid at all temperatures. Nine mols. of phenol to 1 mol. of hexamethylenetetramine give an aggregate which is quite solid and brittle in the cold and a tacky rubbery mass when hot ($170^{\circ}\text{C}.$). Eight mols. of phenol to 1 of hexamethylenetetramine give a mass which is solid at all temperatures, not as brittle in the cold as the 9:1 resin but rubbery when hot, like polymerised tung oil. The more the phenol is reduced the less elastic and resilient the mass becomes when hot, and at the ratio of 5.00–6.5 mols. of phenol to 1 mol. of hexamethylenetetramine the material is quite solid and hard at all temperatures; at room temperatures it is a solid which is not brittle but hard, dense, transparent, and tough, with a tensile strength ranging from 4000–5200 lbs. per sq. inch. When hot it can be dented about like a hard filled rubber. Decreasing the phenol below 5.5–6.5 mols. to 1 hexamethylenetetramine again increases the brittleness of the resin due to the excess of the crystalline hexamethylenetetramine. The product, however, does not melt at any temperature.

RESIN FORMATION.

Statements have been made to the effect that the addition of the proper amount of hexamethylenetetramine to phenols or phenolic resins to form a 6:1 resin produces, on heating, an exceedingly rapid evolution of ammonia and leaves a very porous, spongy mass. This is true in only a limited sense. The rate of the evolution of ammonia may or may not be rapid, depending upon the method of carrying out the experiment. If heated on a water-bath at $100^{\circ}\text{C}.$ for twenty-five hours, less than 50 per cent of the total ammonia will be evolved and the mass is a viscous liquid when hot and a brittle solid when cold.

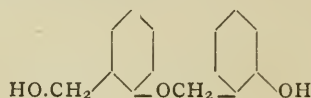
On the other hand, if a 6:1 mixture is heated rapidly at $180^{\circ}\text{C}.$ a spongy material soon forms which may have a volume twenty times that of the original materials. This porous form of the resin is very advantageous when the material is to be pulverised later, since it powders in the ball mill in less than one-tenth the time required to pulverise solid lumps of the resin.

This finely ground material, when pressed in hot moulds under a pressure of 4–6 tons to the sq. in., becomes a homogeneous, transparent solid of maximum mechanical strength, highest dielectric properties, and chemical inertness.

The grinding and moulding of the powdered material in hot moulds, under pressure, is only one of a number of methods which we have in use in this laboratory for producing transparent solid goods. By a simple manipulation of the material, during heating, it is possible to produce large pieces of the final transparent, insoluble resin without the use of external pressure. We have, at present, in our laboratory rods of this material 2 ft. long and $1\frac{1}{2}$ in. in diameter which have been produced by simply pouring the material while liquid into open moulds and allowing it to harden under suitable heat treatment *without the application of external pressure*. These rods in the final condition are homogeneous, almost water white transparent, and free from fractures or gas bubbles.

INTERMEDIATE AND BY-PRODUCTS.

It might at first be supposed that some oxybenzyl alcohols or substituted saligenin would be present at the end of the reaction. This, of course, is impossible when it is remembered that no water is present and all the ammonia has been evolved; oxybenzyl alcohol, saligeno-saligenin, oxybenzylamine, or an amide saligenin are also impossible since there is present in the remaining mass no water or oxygen necessary to form the alcohols, and no nitrogen remains to form the corresponding amines. Such a compound therefore as—



which is probably the second product formed when phenol and formaldehyde react, is impossible when phenol unites with hexamethylenetetramine in the dry. The intermediate products which form may be $\text{NH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{OH}$, $\text{NH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OCH}_2\cdot\text{C}_6\text{H}_4\text{OH}$, $\text{C}_6\text{H}_5\cdot\text{OCH}_2\cdot\text{C}_6\text{H}_4\text{OH}$, &c., but at the end of the reaction the first two products cannot be present as all the nitrogen present in the hexamethylenetetramine has been evolved as ammonia. And as we shall now show the final product which forms in *excess phenol* is a definite compound. This compound has little or no tendency to polymerise or harden and become insoluble on heating, but when mixed with active methylene compounds transforms readily into the infusible resins.

(To be continued).

ON THE TRANSITION TEMPERATURES OF THE HYDRATES OF SODIUM CARBONATE AS FIXED POINTS IN THERMOMETRY.

By THEODORE W. RICHARDS and AUGUSTUS H. FISKE.

RECENT investigations conducted in the Harvard University Laboratory, and confirmed elsewhere, have shown that the transition temperatures of hydrated crystalline salts provide excellent means for fixing definite points upon the thermometric scale.

(NOTE.—T. W. Richards, *Am. Journ. Sci.*, 1898, (4), vi., 201; Richards and Churchill, *Proc. Am. Acad.*, 1899, xxxiv., 277; Richards and Wells, *Ibid.*, 1906, xxxviii., 435; *Ibid.*, 1902, xxviii., 431; Richards and Wrede, *Ibid.*, 1907, xliii., 343; Richards and Kelley, *Ibid.*, 1911, xlvii., 171. Four of these papers are to be found in full in the *Zeit. Phys. Chem.*, the references being respectively, 1898, xxvi., 690; 1899, xxviii., 313; 1903, xliii., 465; 1908, lxi., 313. The work on manganese chloride was finished by Dr. Wrede and one of us at the University of Berlin. The sixth paper appeared also in *Journ. Am. Chem. Soc.*, 1911, xxxiii., 847. Jeannel, *Comptes Rendus*, 1866, lxii., 834, suggested long ago the use of a transition point of hydrated sodium acetate for testing and standardising thermometers, but no one seems ever to have followed up the suggestion or to have actually used it in this way. The fact that such a suggestion concerning any crystalline salt had been made before 1898 has been unknown to the present authors until now. We are indebted to Prof. W. Lash Miller for his having called our attention to it).

The transition temperature of the decahydrate of sodium sulphate at 32.383° was first selected for many reasons, and it has proved to be the most convenient of any as yet studied. (Dickinson and Mueller, *Chemical Abstracts*, 1908, ii., 7, found 32.384° , confirming as nearly as could be expected the value found in this laboratory). Although sodium sulphate is thus to be preferred if only a single point near the ordinary temperature of the room is sought obviously the knowledge of other points would be desir-

able. Accordingly, a number of other substances have been investigated with regard to their suitability for the purpose.

Among the salts suggested in the second Harvard paper (1899) was sodium carbonate. At that time little was known concerning the transition temperatures of the various hydrates of this salt; accordingly, a preliminary determination of one of the points was made, and it was shown that satisfactory constancy was attainable. (Through a typographical error the initial hydrate was stated to contain $10\text{H}_2\text{O}$ instead of $7\text{H}_2\text{O}$ (*Proc. Am. Acad.*, 1909, xxxiv., 278), but this error was eliminated when the paper was reprinted in the *Zeitschrift für Physikalische Chemie*, two months later). The intention was to study this and other points more carefully, but soon afterwards several investigations, especially those by Epple (*Inaug. Diss.*, Heidelberg, 1899), Ketner (*Zeit. Phys. Chem.*, 1902, xxxix., 645), and Wells and McAdam (*Journ. Am. Chem. Soc.*, 1907, xxix., 721), largely covered the ground. These researches, especially the last, have shown clearly that the stable hydrates are the following:—Between -2.1° and $+32.0^\circ$, the decahydrate; between 32.0° and 35.4° , the heptahydrate; and above 35.4° , the monohydrate. Wells and McAdam found also that the transition between the decahydrate and the monohydrate is 32.06° , and their diagram shows very clearly the situation.

Although the work of Wells and McAdam was very carefully done, it seems desirable to verify these points upon as many accurate instruments as possible, and also to determine how well fitted they may be for the standardising of thermometers. If they are easily reproduced, the three transition temperatures would form an exceedingly useful means of calibrating a Beckmann instrument, since they cover three and one-third degree, with an intermediate point. The present paper is concerned with the re-determination of the lowest of the three points.

Purification of sodium carbonate is conveniently conducted by re-crystallisation. The purest "chemically pure" material of commerce was re-crystallised ten times, the transition temperature of each successive group of crystals being taken; the purification was continued until no further change occurred in the transition temperature. The crystallisation was conducted by cooling from about 40° to 10° , and centrifugal draining helped to eliminate the mother-liquor. During the last three crystallisations the substance came into contact only with silver or platinum.

Pure sodium carbonate is not easily kept without deterioration, because it, of course, attracts any trace of hydrochloric or sulphuric or even carbonic acid which may be in the air, either through leakage from stoppers of the laboratory reagent bottles or from the products of combustion of illuminating gas. If the best results are to be obtained from the salt it must be protected with the utmost care, or better, used at once. We have often found that material even preserved over lime or potash for as short a time as twenty-four hours, may change several thousandths of a degree as to its transition temperature, unless the desiccator is well sealed. One of the samples (F), having been kept under a bell-jar not perfectly tight, had its transition point lowered as much as 0.02° in three weeks by impurities taken from the laboratory air. That the salt will keep perfectly pure, when properly guarded, is proved by the very constant results obtained from the purest samples, to be recounted in the following.

The water of crystallisation in the various phases of the salt was determined by titrating weighed amounts of the roughly pulverised crystals (dried in air until just to the point of efflorescing) by means of half normal hydrochloric acid, methyl-orange being used as the indicator. The substance employed in the final determinations showed an average molecular weight of 281, the theoretical molecular weight of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ being approximately 286. After these crystals had been entirely transformed at 32.02° into the

other phase in equilibrium at that temperature, the crystals constituting this new phase were separated from the supernatant mother-liquor, pressed on warm filter-paper in a warm room at about this temperature, and analysed as before. The resulting crystals, when freshly prepared, were found to have a molecular weight averaging 234, leaving no doubt that the phase in question was the heptahydrate, which has a theoretical molecular weight of 238. Pursuing the same quest further, we heated the substance for some time above 40° , when a new phase appeared which was found, after separation of the mother-liquor, to have the molecular weight of 124—thus being without question the monohydrate, which has this theoretical value. All of these phases, on standing in a desiccator over a large excess of concentrated sulphuric acid for three or four weeks, give a substance having a molecular weight below 107, showing that under these conditions the water is practically all removed ($\text{Na}_2\text{CO}_3 = 106$). These conclusions, except the last, all correspond with the statements of Wells and McAdam.

The successive products of the first five re-crystallisations, made from distilled water in porcelain dishes, were all prepared before April 15, 1911, portions of each having been saved for the study of their transition temperatures. After an intermission of a week, two more crystallisations in porcelain were made, and then all of the seven samples were carefully compared as to their transition points.

The preliminary determination of the constancy of the transition temperature was made by means of a sensitive Beckmann thermometer in an apparatus especially like the Beckmann freezing-point apparatus, as indicated in previous papers. The large test-tube containing the salt was surrounded by an air jacket, and this latter was immersed in a water-bath, kept about 0.3° higher than the temperature to be observed by means of a suitable electric coil. The transition point showed a slight and steadily decreasing rise with increasing purity, until sample E was reached. Two subsequent re-crystallisations made no further change in this value—apparently this was the purest salt which could be obtained by re-crystallisation in porcelain. In the meantime the crystallisation was being carried further, from the purest water, in platinum; with this product another constant point 0.001° or 0.002° higher than the preceding was soon reached. This seemed to be the maximum, and therefore the true transition point of the really pure substance.

After the ninth product (sample I) had had its transition point re-determined several times over a period of several weeks, it was re-crystallised once more, and because the corrected reading of the Beckmann thermometer at the transition point of this material gave almost exactly the same value as the preceding, the final determination of the transition temperature was made as soon as possible.

Before the final readings are presented, a tabulated statement of the preceding results may be given; it is of interest as indicating the exact measure of the impurity eliminated in each of the successive steps. One may note that the Beckmann readings needed correction for the pressure (0.002° per centimetre of barometer), and for the temperature of the emergent column (0.001° per degree Centigrade). The comparison of the observed values in the second column and the corrected values in the sixth is not without interest, because it shows how erroneous may be the reading of a sensitive mercury thermometer not thus corrected. The true temperature given in the last column was obtained by adding the quantity 31.628 to each of the readings of the Beckmann thermometer; this quantity was found in the final experiments to be recorded further on.

Complete constancy having thus been obtained, the final temperature readings were made on very exact Baudin thermometers, 15200 and 15276, which have already been described in Harvard papers (*Proc. Am. Acad.*, 1902, xxxviii., 434; *Zeit. Phys. Chem.*, 1903, xliii., 467). Every precaution was taken with the observation, which was made with a very accurate Geneva cathetometer; the

Date. 1911.	Observed.	Bar.	Cor. pres.	° of emergent colum.	Emergent column corrected to 25°.	True temper- ature.
<i>Porcelain Dish.</i>						
April 25	A = 0.309	764.0	0.308	27	0.306	31.934
April 27	B = 0.352	771.0	0.350	28	0.347	31.975
April 28	C = 0.370	760.0	0.370	28	0.367	31.995
April 29	D = 0.380	765.0	0.379	24	0.380	32.008
April 15	E = 0.382	760.0	0.382	19	0.388	32.016
April 24	G = 0.382	758.0	0.382	19	0.388	32.016

<i>Platinum Dish.</i>						
April 24	H = 0.388	763.0	0.387	23	0.389	32.017
April 25	I = 0.389	764.0	0.388	23	0.390	32.018
	0.395	758.0	0.395	30	0.390	
May 12	0.392	757.0	0.393	28	0.390	
May 13	J = 0.394	757.0	0.395	30	0.390	32.017
May 13	0.393	761.0	0.393	29	0.389	
May 15	K = 0.389	761.0	0.389	25	0.389	

thermometers were fixed in a perfectly vertical position, and many readings were made, both from the front and through the back of the stems. Thanks are due to Dr. A. W. Rowe and Dr. G. L. Kelley for their help in making additional readings of these crucial observations. The usual corrections for calibration, internal pressure, external pressure, the fundamental interval, and the average ice point (likewise thus corrected) were applied, as well as further correction for the emergent column. This last was computed in the usual way, and is probably correct to within 0.001° or 0.002°. The final results are tabulated below.

After these determinations, the original Beckmann thermometer was again inserted into the mixture; it then indicated a temperature 0.001° lower than before—an almost negligible difference, perhaps due to impurities taken from the glass and the air during the several hours needed for the exact thermometric readings.

Thus the transition from the dekahydrate of sodium carbonate to the heptahydrate was found to take place at 32.017°. This value is near the reading (32.00°) found by Wells and McAdam, but decidedly higher than the result of Ketner (31.85°). The latter evidently had been less successful in purifying his substances; for impurities usually lower the transition temperature.

The Transition Temperature of Sodium Carbonate : Dekahydrate-heptahydrate.

Designation of thermometer.	15276.	15200.
Observed reading	32.187	32.257
Cor. for calibration	+ 0.006	- 0.005
Cor. for interior pressure	+ 0.056	+ 0.038
Cor. for exterior pressure	+ 0.001	+ 0.001
Cor. for fundamental interval	+ 0.001	+ 0.022
Cor. for corrected ice point	- 0.154	- 0.212
Cor. for emergent thread (a)	+ 0.023	+ 0.020
	32.120	32.121
Cor. to hydrogen scale	- 0.104	- 0.104
Final value	32.016	32.017

(a) 24° of thermometer 15276 and 21° of thermometer 15200 were exposed to the room temperature of 26.0°.

Although this point is quite sufficiently sharp to serve as a means of standardising thermometers, it is probable that the other two points (namely, that involving the dekahydrate and monohydrate, and that involving the heptahydrate and monohydrate) are even sharper and more easily maintained, since, as a rule, other things being equal, an increased latent heat of transition means increased precision. With any given salt, the larger the number of molecules of water lost in transition, the larger

will usually be the latent heat of the change. The transition from the dekahydrate to the heptahydrate observed in the experiment just described involves a loss of only three molecules of water, whereas that from the heptahydrate to the monohydrate means a loss of twice, and that from the dekahydrate to the monohydrate three times as much.

Summary.

In this paper one of the transition temperatures of hydrated sodium carbonate, namely, that between the dekahydrate and the heptahydrate, has been carefully determined with standard instruments, and found to be 32.017° on the hydrogen scale, a value not very much above that of Wells and McAdam, who found 32.00°. Incidentally, the hydrates stable at various temperatures have been analysed, and have been found to correspond to the statements of these investigators. It is shown, moreover, that all of the hydrates lose water easily at ordinary temperatures into air dried by concentrated sulphuric acid, leaving the salt essentially anhydrous, whereas some previous experimenters have thought that one molecule of water still remained under these circumstances.—*Journal of the American Chemical Society*, xxxvi., No. 3.

COLLOIDS AND CRYSTALS, THE TWO WORLDS OF MATTER.

By ROBERT H. BRADBURY,

Head of the Department of Science in the Southern High School,
Philadelphia.

WHEN a solid is brought into contact with a liquid the result depends upon the nature of both. There may be apparently an entire absence of interaction, as when rosin is shaken up with water or chalk with alcohol. Or, as when sugar is agitated with water, the solid may disappear, entering into solution in the liquid. The study of sugar solution shows quite clearly that the connection of the sugar molecules with each other has been completely destroyed. They are dispersed through the water very much as the molecules of a gas distribute themselves uniformly in a vacant space, and in both cases the permanence of the uniform dispersion is due to the incessant motion of the molecules. Were the molecules at rest, both the sugar and the gas would settle and form a layer on the bottom of the containing vessel.

However, the molecules of the sugar retain their structure intact, the action being limited to their dispersion. When salt, on the other hand, is dissolved in water, a further breakdown occurs, the molecule is separated, and ions of sodium and of chlorine move about in the liquid. Both solutions freeze below 0° C. and boil above 100° C. The most important difference between them is that the salt solution conducts the electric current, while the sugar solution is as poor a conductor as water itself.

A fourth possibility presents itself when glue or gelatin is treated with water. The gelatin absorbs water, swells up and, under the influence of heat, dissolves, but the liquid freezes and boils at practically the same temperatures as pure water. The study of the solution shows that the dispersion is not molecular. The particles of gelatin in it are composed of variable and rather large numbers of molecules. A system like this gelatin solution which presents a case of very fine but not molecular subdivision is called a *colloidal solution*. There are certain solids such as gelatin and dextrin (with water), and rubber (with benzene and carbon disulphide), which, when they dissolve in liquids, are invariably dispersed in this way. Such solids may properly be referred to as *colloids*. They are all amorphous. Crystallised substances never yield colloidal solutions by mere spontaneous solution in a liquid. They always produce molecular or ionic dispersions. However, the phenomenon of colloidal solution is perfectly general, and crystallised substances can also be obtained in this condition, but not by mere solution.

It is an interesting fact that a substance which yields a colloidal solution with one solvent may form an ordinary molecular solution with another. Soap is an example. Its concentrated solution in water boils at about 100° , freezes at about 0° , and exhibits the behaviour of a colloidal solution in general. On the contrary, a soap solution in alcohol shows the normal change in freezing and boiling-points corresponding to the molecular weight, and conducts itself in all respects like an ordinary molecular dispersion.

Everyone is familiar with the distinctions between solutions and suspensions. Suspensions are turbid in aspect, and the solid can be removed by letting it settle or by filtration. Solutions are clear, dissolved matter does not subside and is unaffected by filtering. Colloidal solutions occupy an intermediate position.

Consider for a moment the effect of increasing subdivision on a suspension of finely-divided gold in water. So long as the diameter of the particles is much greater than a thousandth of a millimetre, the system will be turbid and the gold will settle rapidly. (It is usual to employ the symbol μ for the thousandth of a millimetre; in the same way, $\mu\mu$ indicates the millionth of a millimetre). But the wave-length of visible light ranges between 0.4μ and 0.7μ , and when the particles become smaller than this they can no longer reflect light and the liquid will appear clear. At the same time there will be a rapid falling off in the speed of settling. Stokes has derived a formula for the velocity of subsidence, V , of small spheres of radius R and density S falling in a liquid of density S' and internal friction f under the force of gravity g :—

$$V = \frac{2}{9} g (S - S') \frac{R^2}{f}$$

Substituting the proper value for gold and water and assuming a radius of μ for the particles, the value for V is about 14 centimetres per hour. This means, of course, that the system would be a coarse suspension and would clear up at once. But when $R = 10\mu$, V is only about a centimetre a month. This begins already to be fairly permanent. It must be remembered that the high density of gold (19.5) increases the rapidity of subsidence. If we make the calculation for $S = 3$, which is about the density of arsenious sulphide, V comes out only about a millimetre a month.

So much for calculation. Now what are the facts. As a matter of fact, the dispersed substance in a colloidal solution does not settle at all, so long as the subdivision is maintained. Colloidal gold solutions have been preserved unchanged for years. I have a solution of arsenious sulphide which has remained apparently unchanged for three years and whose countless particles can readily be seen, engaged in their incessant Brownian movement, with an ordinary oil immersion lens. Whenever settling does occur, it is preceded by the aggregation of the particles into larger particles, which finally attain a diameter of μ or over, and slowly subside.

Here, then, is an apparent discrepancy between Stokes's law and the facts. The law informs us that the speed of subsidence decreases rapidly with decreasing radius of the particles, but it does not lead us to expect the total absence of settling which presents itself when the average radius is 10μ or thereabout.

The explanation, of course, is molecular motion, or, in other words, *heat*. The particles are battered, on all sides, by a hail-storm of molecular impacts. If the particle is large, the blows of the molecules of the solvent in different directions neutralise each other. But when the particle is not so very much larger than the molecules themselves a molecule striking, say on the left, will give the particle a very perceptible push toward the right, "just as a cork follows better than a large ship the motion of the waves of the sea" (Perrin). As the dimensions of the particle approach the molecular dimensions it begins to behave like a molecule and is swept along in the endless molecular movement. The cause which prevents the particles in a

colloidal solution from settling is in no way different from the cause which prevents the earth's atmosphere from subsiding to a snowy layer a few feet deep on the surface of the planet.

It is worth remembering, also, that the particles of the dispersed phase ordinarily possess an electric charge, which is usually negative. The effect of the repulsion of these similar charges would be to preserve the distribution of the particles throughout the liquid. It is a fact that, when the charges are removed, the system becomes unstable and subsidence—preceded by coalescence of the small particles—readily, but not necessarily, occurs.

On the subject of the classification of colloid systems we must be very brief. One proposal subdivides them into *suspensoids*, such as the sols (Thomas Graham introduced the term sol as an abbreviation for colloidal solution) of gold and arsenious sulphide, in which the dispersed phase is solid, and *emulsoids*, in which the dispersed phase is liquid. This classification would appear to be an attempt to extend the familiar distinction between liquid and solid to a domain in which that distinction has little if any meaning. To assert that a thing is solid is to say that it has a definite shape, which it retains with some persistence. There is not the slightest reason to think that the particles in a gold sol are solid. It is usual to assume that they are spherical, but this is done merely because it is the simplest assumption to make. There are faint indications that they really have the form of leaflets or of little rods, but they appear in the ultra-microscope simply as brilliant dancing points, and in reality we know nothing whatever about their shape. In connection with this it is interesting to recall the fact that the formation of a crystal begins with the appearance of minute liquid spheres, globulites (Fink, *Pogg. Ann.*, 1839, xlvii., 258; Schmidt, *Liebig's Ann.*, 1845, liii., 171; Frankenheim, *Pogg. Ann.*, 1860, iii., 1), which pass through several stages (margarites, longulites, &c.) before the crystal is formed. It seems possible that, under such enormous subdivision, cohesion retires into the background and surface tension assumes the chief rôle, so that the gold particles are rather to be compared to minute drops than to little crystals.

Enough has been said to make clear the uncertainty which attaches to the attempt to classify colloid solutions according to the state of aggregation of the particles. A better classification is into *reversible* and *irreversible* colloids, according to the way in which the dissolved substance behaves when separated from the solution. Thus, when a gelatin solution is evaporated until it "sets" it is only necessary to warm the jelly with water to obtain it again in colloidal solution. Gelatin is a typical reversible colloid. But when the gold is caused to separate from a gold sol—which can easily be brought about by adding any electrolyte to the sol—the gold will not again enter into colloidal solution. Shaking or warming with water gives a mere suspension, which settles at once. Gold is an *irreversible* colloid. The distinction is fundamental. Many organic colloids are reversible, while it is rather the habit of the inorganic colloids to behave in the irreversible way.

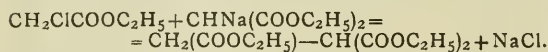
In order to prepare a sol containing an irreversible colloid all that is necessary is to reduce the solid to extreme subdivision in a liquid in which it is insoluble. The electric arc furnishes a rapid and simple method (Bredig, *Zeit. Angew. Chemie*, 1898, p. 951; for a full account of Bredig's work with the platinum sol, see *Zeit. Phys. Chem.*, 1899, xxxi., 258–353). Two gold wires about 2 mm. thick are connected with a 220-volt circuit and brought together under distilled water. A 110-volt circuit can be used, but more patience is required. Sols of platinum, silver, copper, and other metals can be made in the same way. By related electrical methods, using such liquids as pentane and anhydrous ether, Svedberg (*Ber.*, 1905, xxxviii., 3616) obtained sols of all five of the alkali metals. The colours of the sols agreed with those of the vapours of the corresponding metals.

Chemical reduction of a salt of a metal furnishes another method which has been largely employed by Zsigmondy (see his monograph, "Zur Erkenntnis der Kolloide," Jena, 1905, which has been translated by Jerome Alexander) and other investigators. For instance, a very dilute solution of auric chloride is mixed with such reducing agents as formaldehyde, hydroxylamine, or an ethereal solution of phosphorus. The gold sols obtained in this way are usually red by transmitted light, the particles being bright green and very much smaller than in the sols obtained by the electrical method.

By various chemical methods, which lack of space forbids us to discuss, sols of sulphides (CdS , As_2S_3 , Sb_2S_3 , &c.) and oxides (Fe_2O_3 , Al_2O_3) can be obtained. The sol of aluminium oxide is important on account of its connection with dyeing and mordanting. The formation of the blood-red sol of ferric oxide by adding a concentrated solution of ferric chloride to about 50 volumes of boiling distilled water is a simple and beautiful lecture experiment.

In making colloidal solutions of salts, the essential thing is to mix dilute solutions of the precipitants, using a liquid in which the insolubility of the product is as complete as possible. Thus, in mixing very dilute solutions of sodium sulphate and barium chloride, a crystalline precipitate is usually obtained. The reason is that barium sulphate possesses a very slight but real solubility in water. Hence the liquid in contact with the particles first formed contains enough barium sulphate to nourish their growth and allow them to develop to crystals. If alcohol is added to the sulphate, before the barium chloride is introduced, the solubility of the barium sulphate is greatly reduced, and it is obtained in colloidal solution without difficulty.

In the same way, if we mix water solutions of sodium hydroxide and of hydrochloric acid we obtain merely an ordinary solution of common salt. But if salt is produced by reaction between organic compounds in a liquid in which the sodium chloride is insoluble, then a colloidal solution is obtained. For instance, when chloro-acetic ester interacts with sodio-malonic ester a greyish opalescent sol of sodium chloride in ethenyl tricarboxylic ester results.



At low temperatures, in such liquids as toluene and chloroform, even ice has been obtained in colloidal solution.

The most striking property of the reversible colloids is that they are able to communicate their reversibility to the irreversible ones. Thus, if a trace of gelatin is added to a gold solution, the gold becomes much more difficult to coagulate by electrolytes, and when coagulated it can be dispersed again by merely warming with water. This curious protective action is exerted, in greatly varying degree, by most reversible colloids. Direct study of the phenomenon with the ultra-microscope shows that the view frequently expressed that the gelatin envelops or forms a film around the gold particles is incorrect. What actually happens seems to be a direct combination between gelatin particles and gold particles, which then pass through the reversible changes together.

Protective colloids enjoy a wide practical application. In the manufacture of photographic films the gelatin retards the crystallisation of the silver bromide. Ink often contains a colloid which prevents the pigment from settling. The lubricant "aqua dag" put in the market by the Acheson Co. consists of finely-divided artificial graphite, held up by a protective colloid. Clay is made plastic for the potter by an empirical process which involves the action of protective colloids derived from decaying vegetable matter. The addition of gelatin in making ice cream depends upon its protective action in preventing the growth of ice crystals, which would make the product "gritty." Without doubt protective action plays an important rôle in the cleansing action of soap. This has been made clear by some recent experiments of Spring (*Kolloid Zeit.*, 1909, iv., 161; 1910, vi., 11, 109, 164). Lampblack, freed from oil by long washing with alcohol, ether, and benzene,

forms a rather stable suspension in water, but the lampblack is detained by a paper filter. If the filter is now reversed, so that the blackened surface is outward, and water poured through it, the lampblack is not removed, but a dilute soap solution removes the coating and cleanses the filter at once. Finally, lampblack suspended—or colloidally dissolved—in soap solution, passes through a filter unchanged. It is of much practical interest that there is a well-marked optimum in the concentration of the soap required to protect the lampblack. A 1 per cent soap solution is the most efficient. In 2 per cent soap solution lampblack sinks about as rapidly as in pure water.

We have already considered the probable actual condition of the particles in a colloidal solution and have concluded that, for the present, no very definite information is obtainable about the matter. We must now return, for a moment, to the subject in order to allude to the thesis so brilliantly advocated by van Weimarn, the Russian investigator, who holds that the particles are of necessity minute crystals and that there is, in fact, no such thing as amorphous matter. He even goes so far as to state the substances like air and water are in a "dynamic cryptocrystalline condition," though I have been unable to understand what he means by this statement.

Briefly, the evidence that van Weimarn adduces to the support of his hypothesis is:—

1. That colloid particles will grow to crystals if provided with the proper nourishment, namely, a dilute solution of the same substance.

2. That colloid particles are capable, when introduced into a supersaturated solution of the same substance, of discharging the supersaturation and inducing the formation of crystals.

Those who desire to follow this matter further should read van Weimarn's little book, "Grundzüge der Dispersoidchemie," after which they will find themselves very much interested, but somewhat unconvinced. Let me hasten to add that I have not the least desire to undervalue the brilliant experimental work of the Russian chemist. It is, in fact, precisely by the conception of more or less daring hypotheses, and the working out of their consequences, that our science achieves its endless victory over the nescience about us.

We have seen that the wave-lengths of the visible radiations are comprised between 0.4μ and 0.7μ . With objects much smaller, the ordinary microscopic method ceases to be applicable. Using ultra-violet radiation for illumination quartz lenses in the microscope, and receiving the image with the photographic plate instead of the eye, it is possible to advance a step further in the domain of the infinitesimal, but only a step, and there are obvious objections to the proceeding. Since some of the particles in colloidal solutions are only 0.006μ in diameter, we can never hope to see them as little bodies subtending a visual angle. The ultra-microscope—the powerful instrument of investigation to which most of our knowledge of colloid systems is due—renounces this idea, and makes the particles visible merely as glittering points on a black background. The sol is placed in a small rectangular glass trough and a horizontal beam of arc light or sunlight focussed in it. The microscope is placed vertically above the trough. It will at once be seen that there are two fundamental things about the instrument, to provide intense illumination, and to make sure that no light enters the microscope except the rays which emanate from the particles. The principle is simple, but the system of diaphragms and lenses needed to secure the second object makes the ultra-microscope an elaborate and expensive instrument in practice.

Cotton and Mouton achieved the same end in a different way (*Comptes Rendus*, 1903, cxxxvii., 1657). The illumination (arc or sunlight) is thrown up from below by a paraboloid reflector so ground that all rays, *except those diffracted by the particles*, are totally reflected from the cover-glass over the sol. This instrument is simple, easily adjusted, and cheap. It is made commercially by

the firm of Zeiss. It would seem to be admirably adapted to school purposes. In fact, after a look into the ultra-microscope, the study of the molecular topics ceases to be drudgery and becomes a positive intellectual need.

Even a brief glance at the subject of colloid systems must at least mention the classic work of Perrin on the distribution of the particles in suspensions of gamboge and mastic (*Ann. Chim. Phys.*, 1909, 3rd Series, xviii., 5; there is a German translation by Donau in *Kolloid-chemische Beihefte*, 1910, i., 1; an English translation by Soddy has appeared in book-form under the title, "The Brownian Movement and Molecular Reality"). He succeeded, by an ingenious and simple method, in preparing emulsions of gamboge in water in which the spherical yellow granules were all of the same diameter. If we consider a mass of such a liquid in a tube, it is clear that the granules, if at rest, would, since they are denser than water, all fall to the bottom. The fact that they remain suspended is due to their movement. In other words, the state of things is the same as in the earth's atmosphere, and just as the molecules are more crowded near the earth's surface, so the granules of gamboge must be more numerous near the bottom of the liquid than in the upper layers. Perrin verified this prediction by direct counting of the granules under the microscope. The barometric formula which describes the progressive rarefaction of air with increasing height also describes the distribution of the granules in Perrin's uniform emulsions. The only difference is that, while the aviator must ascend six kilometres in order to reach air half as dense as at sea level, the same effect is produced in Perrin's emulsion by an ascent of 0.1 mm.

That the mean energy of rotation of a molecule must be equal to its mean energy of translation is one of the chief propositions of the kinetic theory. Perrin has proved this by direct measurement of the rotation of granules under the microscope. For this purpose, large granules (15 μ) of mastic were employed. These are far too heavy to remain suspended in water, so a solution of urea was used. Fortunately, the granules contain little inclusions which make it possible to measure their rotation.

These are only two of many fundamental results contained in this wonderful memoir. Van't Hoff extended the gas laws to solutions. Perrin has now proved them to be valid for systems in which the moving particles are visible realities. Let us end by quoting one of the sentences of his conclusion:—

"La découverte de telles relations prouve le point où s'élève, dans notre conscience scientifique, la réalité moléculaire sous-jacente."—*Chemical Engineer*, xix., No. 2.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

At the last sitting of the Academy of Sciences, Prof. Dastre, in the name of M. Pierre Girard, assistant at the laboratory of physiology of the Sorbonne, gave a notice on the hemipermeability of the cellules to the ions. The researches of M. Pierre Girard establish that the globules of the blood taken as types of living cellules are permeable electively to the ions of the electrolytes present in the inner environment and not to the molecules. In given conditions their permeability for one of the ions of a salt contained in the inner environment may be considerable, whereas their permeability for the ion of an opposed electric sign is very weak. The apparent choice that the living cellule seems to make among the elements of the interior environment is with the synthetical power of the protoplasm the striking feature of elementary life. In his new work M. Pierre Girard shows that, as far as the ions are concerned, the mechanism of this elective permeability has nothing vital in it. It is electrostatic, and depends on the state of polarisation of the walls of the globules. *In vitro* a thin membrane of gold-beater's

skin separating, for example, from pure water a solution of chloride of barium containing a slight excess of hydrogen ions, is polarised, and the electric field of which it is the seat operates among the ions, bearers of charges of signs opposed to the chloride of barium, diffusing towards the water; for a given orientation of the field of polarisation (corresponding, for example, to a slight excess of hydrogen ions in the solution of chloride of barium), the passage of chlorine ions will be favoured, and the issue of barium ions rendered difficult; for an inverse orientation of the fields of polarisation it will be the passage of the barium ions that will be favoured. This is a pretty exact image of what takes place in the living organism. The walls of the living cellules, which separate the intercellular from the natural environment, are polarised; the sign of the charges with which their exterior face is covered when they are free is discovered by the displacement of the cellules in an electric field; it is on the field of polarisation of the cellular wall, on its value, and its orientation that, it appears, depends its hemipermeability, which is besides related to the ions. It is easy to modify this permeability towards a given ion in inverting the sign of the charges of the cellular walls by the addition of an environment of suspension of hydrogen ions.

THE CONGRESS FOR THE ADVANCEMENT OF SCIENCE.

The opening meeting of the Forty-third Congress of the French Association for the Advancement of Science was held in the Grand Theatre of Hâvre on Monday, July 27, and was presided over by Prof. Armand Gautier, member of the Institute of France and of the Academy of Medicine. A large number of learned men, doctors, and hygienists came from all parts of the country to be present at the Congress. This year these scientific meetings are exceptionally brilliant, the elder sister of the Association Française for the Advancement of Science, the British Association, having decided to take part in the French Congress. Whereas a certain number of English savants have gone to Australia to the congress of the British Association, many others have decided to join the French colleagues and to come over and participate in the scientific discussions at Hâvre. Sir William Ramsay, member of the Royal Society and of the French Institute, Sir George Fordham, and Prof. Willem, of Ghent, have been specially invited by the City of Hâvre, and the British Association has delegated forty English savants to be present at the Congress. Prof. Armand Gautier opened the session in a very important speech. He mentioned that this is the second time in forty-three years that the French Association met at Hâvre. Following an essentially patriotic aim in 1872, the founders of the Association decided that they would meet every year on different points of the French territory with the harvest of their works and personal ideas. In his opening speech the president is traditionally obliged to treat of some subject concerning his own scientific work, or that of interest to the region in which the Association is holding its congress. Prof. Gautier took as his subject "The Sea that Bathes Our Coasts over More than 2700 Kilometres." After having shown how the sea, which seemed destined to separate men for ever, has become through their audacity the high road of civilisation, M. Armand Gautier shows how the sea interests us from various other points of view. In 1905, says he, at the Congress of Hydrology of Venice, I, for the first time, made known my views on the origin of thermo-mineral waters which have since been almost universally accepted. I tried to show how most of our thermo-mineral waters, far from originating in the rain-water, which penetrating into the depths of the earth would there become heated and mineralised before rising again to the surface, are not of superficial origin. If the rain has its origin in the sea the same cannot be said of the sea, which has not its origin in rain. The sea, in the past, came forth from the incandescent bowels of the earth. And since, as everything indicates, like most

thermo-mineral waters, the sea is an igneous product, it must also contain the substances which characterise these waters. Indeed, in the sea are to be found not only sea-salt, potash, so precious for agriculture, magnesia, iodine, bromine, but also phosphorus, boracic acid, fluor, and still more rare bodies, such as copper, silver, gold, observed by Forchhammer, though it is true these bodies are found in too small quantities for them to be made any use of. But the sea is an inexhaustible source of other industrial products. To draw from the beds of the ocean the food necessary to man no tilling or sowing are required, the plankton is unceasingly working for us.

THE SOUTHERN SHETLANDS.

The mineralogical constitution of the Southern Shetlands has just been the object of a study by M. Gourdon, a mineralogist of the Second French Antarctic Expedition commanded by Dr. Charcot. In a communication presented to the Academy by Prof. Lacroix, M. Gourdon studies especially the King George Island and Bridgman Island. This latter is only a fragment of a volcanic upheaval, now disappeared. In the open sea it forms a pyramid of projected material traversed by torrents of lava. The chemical analysis of the rocks that have been brought back from the Shetlands shows a high proportion of lime and alkali with a predominance of soda over potash.

A PHOTOGRAPHIC MICRO-AMPEREMETER.

M. Albert Turpin, Professor at the Faculty of Science of Poitiers, was the first to succeed in 1912 in obtaining the graphic registrations of time signals transmitted by wireless telegraphy. In a paper presented by M. d'Arsonval, M. Turpin indicates that he has realised two new types of apparatus. One allows of the reception of meteorological and other radio-telegrams; the other permits the precise study of diverse wave detectors. M. Turpin has been able to discover that the time tops of the Eiffel Tower have a slight irregularity, that reaches and may exceed a millionth of a second.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

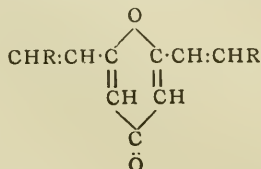
Ordinary Meeting, June 18, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President,
in the Chair.

(Concluded from p. 72).

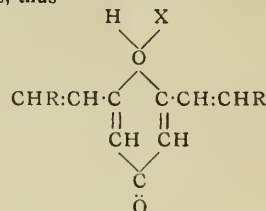
188. "The Constitution of the Arylidenedimethylpyrones and their Salts." By ALFRED ARCHIBALD BOON, FORSYTH JAMES WILSON, and ISIDOR MORRIS HEILBRON.

The authors have examined the absorption spectra of bis-*p*-methoxybenzylidenedimethylpyrone, bisbenzylidenedimethylpyrone, and bisfurfurylidenedimethylpyrone. They find that the absorption curves of these substances are all practically identical, and, moreover, are very similar to the curve of the alcohol compound of dimethylpyrone. They therefore conclude that the arylidenedimethylpyrones possess symmetrical formulæ of the type—



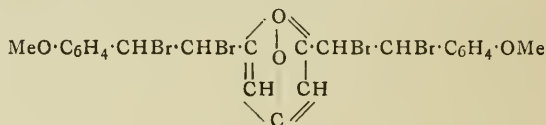
The absorption curves of the salts which these arylidenedimethylpyrones form with acids show two bands, a small colour band with head about λ 1/2200, and a large well-defined band quite similar in intensity and position to the

parent substances. The authors therefore believe that these salts are structurally similar to the free arylidenedimethylpyrones, thus—



(X = acidic radicle).

On bromination, bis-*p*-methoxybenzylidenedimethylpyrone yields a tetrabromo-additive product, which does not form salts with acids, and, like dimethylpyrone, shows only general absorption. Accordingly the authors ascribe to this compound the bridged structure—



The addition of bromine apparently has the effect of making the whole molecule too acidic for salt-formation with acids, as is the case with diacetyldimethylpyrone (compare Collie, *Trans.*, 1904, lxxxv., 971).

The authors conclude from these results that acidic or weakly basic pyrones, such as those examined by Baly, Collie, and Watson (*Trans.*, 1909, xcv., 144), possess bridged structures, whilst the arylidenedimethylpyrones, which are more basic in character, yielding as they do stable salts with acids, possess symmetrical structures.

189. "The Constituents of the Flowers of *Anthemis nobilis*." By FREDERICK BELDING POWER and HENRY BROWNING, jun.

The material employed for this investigation consisted of the flower-heads of *Anthemis nobilis*, Linné, collected from plants grown in Belgium.

Apart from the essential oil yielded by distillation with steam, the flowers were found to contain the following definite compounds:—(1) 3:4-dihydroxycinnamic acid; (2) apigenin, $\text{C}_{15}\text{H}_{10}\text{O}_5$; (3) a glucoside of apigenin, $\text{C}_{21}\text{H}_{20}\text{O}_{10} \cdot \text{H}_2\text{O}$, which yields an hexaacetyl derivative, $\text{C}_{33}\text{H}_{32}\text{O}_{16} \cdot 4\text{H}_2\text{O}$; (4) choline, $\text{C}_5\text{H}_{15}\text{O}_2\text{N}$; (5) *i*-inositol, $\text{C}_6\text{H}_6(\text{OH})_6$; (6) triacontane, $\text{C}_{30}\text{H}_{62}$; (7) taraxasterol, $\text{C}_{29}\text{H}_{47}\text{OH}$; (8) a phytosterolin (m. p. 280–283°); (9) a mixture of fatty acids, consisting of cerotic, stearic, palmitic, oleic, and linolic acids. The flowers contained, furthermore, a considerable quantity of sugar, which yielded *d*-phenylglucosazone (m. p. 208–210°). The amount of fatty and resinous material, from which some of the above-mentioned substances were obtained, was equivalent to about 7.4 per cent of the weight of flowers employed.

The bitter taste of chamomile flowers appears to be due to dark coloured, amorphous material, and not to any well-defined constituent.

190. "The Constituents of *Clematis vitalba*." By FRANK TUTIN and HUBERT WILLIAM BENTLEY CLEWER.

The material employed for this investigation consisted of the flowering branches of *Clematis vitalba*, Linné, which had been specially collected for the purpose.

Preliminary tests showed the absence of any alkaloid, and that only a trace of volatile material was present.

An alcoholic extract of the dried and ground material yielded, in addition to much chlorophyll and resin, the following definite compounds:—(1) 3:4-dihydroxycinnamic acid; (2) caulapogenin, $\text{C}_{42}\text{H}_{66}\text{O}_6$; (3) a saponin, $\text{C}_{54}\text{H}_{86}\text{O}_{16}$, which proved to be a new glucoside of caulapogenin; (4) dextrose; (5) myricyl and ceryl

alcohols; (6) hentriacontane, $C_{31}H_{64}$; (7) a phytosterol; (8) a phytosterolin, which apparently consisted essentially of stigmaterol glucoside; (9) melissic, cerotic, and palmitic acids, together with a mixture of unsaturated acids, consisting largely of linolic acid, and an acid, $C_{22}H_{44}O_2$ (m. p. 69.5°), apparently isomeric with behenic acid.

The statements regarding the irritant properties of *Clematis vitalba* cannot be confirmed.

191. "A Magnetic Study of Compounds of Water and of Aqueous Solutions." By FRANCIS WILLIAM GRAY and WILLIAM MILNE BIRSE.

For the constitution of compounds like copper sulphate pentahydrate, suggestions based on magnetic measurements were made, and a magnetic study of benzoic, phthalic, maleic, succinic, and camphoric acids and their anhydrides was also described. The magnetic properties of solutions were discussed, and it was shown that aqueous potassium ferricyanide solutions obey the law of additivity throughout the whole range of concentrations. A value for the susceptibility of potassium ferricyanide is thus obtained.

192. "The Rate of Combination of Gaseous Nitric Oxide and Chlorine." By JOSEPH EDWARD COATES and ADA FINNEY.

A study has been made of the kinetics of the gas reaction $2NO + Cl_2 = 2NOCl$, which proceeds with measurable velocity at the ordinary temperature. Known quantities of pure chlorine and nitric oxide were rapidly mixed in a glass bulb kept at constant temperature, and the gradual change of pressure at constant volume was followed by means of a mercury manometer connected with the reaction-vessel by a glass capillary tube filled with nitrogen. On mixing the gases, the temperature rose a few degrees, but soon fell to a constant value. The reaction was half completed in about five to six minutes. Satisfactory velocity constants were obtained only by the use of an equation for reactions of the third order. This is in agreement with the ordinary chemical equation, and constitutes a well-defined example of a "pure" (the walls of the vessel are almost certainly without influence) gas reaction of the third order; such reactions, as is well known, are extremely rare.

193. "Carajura and Chica Red." (Preliminary Note). By ARTHUR GEORGE PERKIN.

"Carajura," a rare pigment, considered to be identical with "Chica red" (compare Erdmann, *Fahresber.*, 1857, 487), is said to be prepared by the Indians of Central America from *Bigonia chica*. The material examined, obtained through the kindness of Messrs. Wright, Layman, and Umney, contains a small quantity of the calcium compounds of at least two colouring matters, which have either been precipitated on, or intermingled with, a substance of the nature of ground bark or peat. After treatment with hot dilute hydrochloric acid, alcohol removes the colouring matters in the form of a resin, and from this, by means of boiling benzene, *carajurin* is isolated. This compound, to which the formula $C_{18}H_{16}O_5$ has been provisionally assigned (found, $C = 60.09$; $H = 5.28$), separates in ruby needles, melting at $204-206^\circ$, soluble in boiling dilute alkali with a red colour, and is nearly devoid of dyeing properties. With mineral acids, it very readily yields oxonium salts, crystallising in bright, orange needles, of which the sulphate, probably $C_{18}H_{16}O_5 \cdot H_2SO_4 \cdot H_2O$ (found, $C = 50.67$; $H = 4.35$), is the most stable, the hydrobromide and hydrochloride being decomposed at 100° . From the hydrochloride, a platinum-chloride was prepared. Cold acetic anhydride with a trace of pyridine, after two days, gives an almost colourless acetyl compound, crystallising in needles, whereas bromine gives an immediate precipitate with carajurin in acetic acid, which, when boiled with this solvent, separates in orange needles. Hydriodic acid converts carajurin, with loss of two molecules of methyl iodide, into *carajuretin* hydriodide, bright scarlet needles, stable in the presence of

cold water, and from this, by means of cold pyridine, *carajuretin*, probably $C_{16}H_{12}O_5$, scarlet needles melting above 330° , and soluble in alkalis with a reddish-violet colour, is produced. By dry distillation, carajurin evolves a trace of aromatic oil, resembling anisaldehyde in odour, and when fused with alkali, *p*-hydroxybenzoic acid, and a colourless substance, melting at $185-187^\circ$, as yet unidentified, are obtained. In many respects carajurin resembles the anhydrohydroxybenzopyranol compounds described by Bülow and Wagner (*Ber.*, 1901, xxxiv., 1199).

That portion of the alcoholic extract insoluble in benzene yields to ether *carajurone*, isolated as a scarlet powder, which readily assumes a beetle-green lustre, and possesses strong dyeing properties. Analysis indicates the presence of more oxygen in this compound than in carajurin. A small amount of a similar, but brighter, lake from British Guiana, and obtained from the leaves of a "bushrope," gave a colouring matter dyeing also alizarin-like shades. This lake, considered to be "chica red," appears to differ in some respects from the "carajura" above described.

194. "The Interaction of Nitric Acid and the Sulphides of β -Naphthol." By CHARLES GRAHAM HUTCHISON and SAMUEL SMILES.

When treated with nitric acid under suitable conditions, naphthasulphonium-quinone yielded a mononitro-derivative, which was converted into a phenylhydrazone and into chloronitronaphthathioxin. Interaction of the isosulphide and nitric acid furnished the same nitro-quinone in almost quantitative yield, but the normal sulphide, even under mild conditions, gave only a very small quantity of this nitro-compound with a relatively large amount of dinitro- β -naphthol. Experiments were also quoted to show that the conversion of either sulphide into the quinone involves a loss of two atoms of hydrogen per molecule.

195. "Dinaphthathioxonium Salts." By BROJENDRANATH GHOSE and SAMUEL SMILES.

It was shown that, whilst acetyl chloride reacts with naphthasulphonium-quinone, yielding chlorodinaphthathioxin, acetyl iodide furnishes *dinaphthathioxonium iodide*. The latter substance was converted into dinaphthathioxin by means of sodium thiosulphate. Other salts of dinaphthathioxonium were obtained by interaction of acids and the corresponding sulphoxides, the change being parallel to that previously observed in the phenazothionium, carbothionium, and thiothionium series.

The following note has been received since the meeting:—

196. "Alizarin α -Methyl Ether." By JOSEF OESCH and ARTHUR GEORGE PERKIN.

Alizarin α -methyl ether, which is present in Chay root, *Oldenlandia umbellata* (*Trans.*, 1893, lxiv., 1160; 1907, xci., 2068), and contains the methoxy-group in the peri-position with respect to the carbonyl group, has been prepared in small quantity by the action of an ethereal solution of diazomethane on a nitrobenzene solution of monoacetylalazarin and subsequent removal of the acetyl group (*Trans.*, 1899, lxxv., 447). It was obtained in needles melting at $117-178^\circ$, gave the acetyl compound melting at $211-213^\circ$, and possessed the characteristic properties of the natural product.

CORRESPONDENCE.

COLLOIDS.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS of July 24 (vol. cx., p. 44), in an article reprinted from the *Chemical Engineer*, the following occurs:—"Thus Picet and Lume, working under Ramsay . . ." Is this meant for Linder and Picton, whose papers appeared in the *Journal of the Chemical Society*?—I am, &c.,

CHAS. E. FRANK.

NOTICES OF BOOKS.

Roger Bacon. *Essays Contributed by Various Writers.* Oxford: The Clarendon Press. 1914.

THIS book contains a collection of essays written in commemoration of the seventh centenary of Roger Bacon's birth, and is issued by the Executive Committee appointed to organise the celebrations of the event. The writers of the Essays are men of international reputation, and students of Bacon's works and of thirteenth century science will welcome the opportunity of reading short summaries of his remarkable contributions to various branches of knowledge. Some of the essays have been written by German and French authorities, and are printed in these languages; thus Dr. L. Baur discusses the influence of Robert Grosst te upon Bacon, and Prof. Pierre Duhem writes on Bacon's views concerning Nature's abhorrence of a vacuum. His place in the history of mathematics and his relations to alchemy and chemistry are treated by Prof. D. E. Smith, of Columbia University, and by Prof. M. M. Pattison Muir respectively, and one of the most interesting of the essays discusses the question of his supposed invention of gunpowder, which the author, Col. H. W. L. Hime, suggests was rather an accidental discovery than an invention.

Production of Temperature Uniformity in an Electric Furnace. By A. W. GRAY. Washington: Government Printing Office. 1914.

IN this paper the author gives an account of the method he has devised of uniformly heating a region of considerable length up to a temperature of about 700°. He uses an electric furnace of special construction closed by a double plug formed of two thick blocks of a good heat conductor separated by a comparatively long layer of a poor conductor. The tables and diagrams showing the results of the determinations of temperature distributions in consecutive trials show the efficacy of the method, and with a bar 30 cm. long it was found that after the furnace had been started in the late afternoon and left to itself overnight the mean temperature did not differ by more than 0.16° from that at the centre.

Les Pierres Pr cieuses. ("Precious Stones"). By JEAN ESCARD. Paris: H. Dunod and E. Pinat. 1914. (30 fr.).

THIS treatise on the properties, distribution, and use of precious stones is one of the most comprehensive in existence in any language. It is intended not only for geologists, mineralogists, and chemists, but also for prospectors, who will find in it copious details of all known deposits and strata containing precious stones. For the benefit of lapidaries and jewel workers descriptions of the working of gems are given, and the determinations of precious stones by simple methods is fully treated. One chapter is given to an account of the artificial production of gems, and methods of detecting imitations are also described. The volume is very well illustrated, and some good colour plates are provided.

Der Nachweis Organischer Verbindungen. ("The Identification of Organic Compounds"). By Dr. L. ROSENTHALER. Stuttgart: Ferdinand Enke. 1914.

THE identification of organic compounds is a problem of growing importance in chemistry, and one which is beset with difficulties owing to the lack of systematic methods. This treatise on the subject will undoubtedly fill a gap in German scientific literature. The author has brought together from many sources all available material relating to the identification of the more important organic compounds, and has to some extent amplified it by the addition of his own personal observations and researches. The book, which is by far the largest of the series on chemical

analysis edited by Dr. B. M. Margosches, contains descriptions of the physical properties of compounds and gives copious details of their identification and separation from allied compounds. Melting-point tables are included, and no important method appears to have been overlooked. With the aid of the treatise the chemist should have no difficulty in attacking the qualitative investigation of a mixture of organic compounds or the identification of any substance, and the whole subject is clearly treated upon a sound theoretical basis.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvii., No. 8, 1914.

Compounds of Nitric Oxide with Ferrous and Cupric Salts.—W. Manchot.—If an alcoholic solution of iron chloride is saturated with nitric oxide at 0° and ammonium phosphate, (NH₄)₂HPO₄, is added, a dark brown precipitate is obtained. This precipitate is ferrous-nitric oxide phosphate, (FeNO)HPO₄. Under the microscope it is seen to consist of small crystals, and it is the first representative of the series of compounds which has been obtained in the solid crystalline state, and which contains a molecule of nitric oxide to an atom of iron. The powers of combining with NO is limited in the case of copper salts to the sulphate, chloride, and bromide. These all combine with one molecule of nitric oxide according to the reversible reaction CuR₂ + NO ⇌ CuR₂NO.

MISCELLANEOUS.

Solubility in Water of Nitrate Compounds of Calcium Cyanamide.—C. Manuelli.—The nitrate compounds of calcium cyanamide dissolve rapidly in water, and after an hour 80 per cent of the total nitrogen has passed into solution. After the first hour solution proceeds only very slowly, and at the end of six hours 88 per cent of the total nitrogen, and after eight hours 90 per cent, is dissolved. The quantity of nitrate dissolved then diminishes slightly, evidently owing to the transformation of cyanamide into comparatively insoluble dicyanamide.

International Exhibition, Montreal, 1917.—The May June number of the *Revue Economique Canadienne* contains some general information relating to the proposed universal and international exhibition to be held at Montreal in 1917 in commemoration of the formation of the Canadian Confederation. The moral and material advantages derived from exhibitions are discussed by the director of the Ecole des Hautes Etudes, and some objections which may be raised against the plan are foretold and answered. It is naturally too early to give any details of the size and scope of the exhibition, but should the plan come to maturity there seems to be every reasonable prospect of its being well supported on all sides.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Fire and Acid Proof Materials.—A correspondent asks for the title of books on the following subjects:—(1) Heat resisting materials with reference to furnace linings, e.g., fireclay, gannister, &c.; (2) acid resisting materials for retorts containing acids.—W. D. S.

THE CHEMICAL NEWS

VOL. CX., No. 2856.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

AUSTRALIA, 1914.

INAUGURAL ADDRESS OF THE PRESIDENT, Prof. WILLIAM BATESON, M.A., F.R.S.

PART I.—MELBOURNE.

THE outstanding feature of this Meeting must be the fact that we are here—in Australia. It is the function of a President to tell the Association of advances in science, to speak of the universal rather than of the particular or the temporary. There will be other opportunities of expressing the thoughts which this event must excite in the dullest heart, but it is right that my first words should take account of those achievements of organisation and those acts of national generosity by which it has come to pass that we are assembled in this country. Let us, too, on this occasion, remember that all the effort, and all the goodwill, that binds Australia to Britain would have been powerless to bring about such a result had it not been for those advances in science which have given man a control of the forces of Nature. For we are here by virtue of the feats of genius of individual men of science, giant-variations from the common level of our species; and since I am going soon to speak of the significance of individual variation, I cannot introduce that subject better than by calling to remembrance the line of pioneers in chemistry, in physics, and in engineering, by the working of whose rare—or, if you will, abnormal—intellects a meeting of the British Association on this side of the globe has been made physically possible.

I have next to refer to the loss within the year of Sir David Gill, a former President of this Association, himself one of the outstanding great. His greatness lay in the power of making big foundations. He built up the Cape Observatory; he organised international geodesy; he conceived and carried through the plans for the photography of the whole sky, a work in which Australia is bearing a conspicuous part. Astronomical observation is now organised on an international scale, and of this great scheme Gill was the heart and soul. His labours have ensured a base from which others will proceed to discovery otherwise impossible. His name will be long remembered with veneration and gratitude.

As the subject of the Addresses which I am to deliver here and in Sydney I take *Heredity*. I shall attempt to give the essence of the discoveries made by Mendelian or analytical methods of study, and I shall ask you to contemplate the deductions which these physiological facts suggest in application both to evolutionary theory at large and to the special case of the natural history of human society.

Recognition of the significance of heredity is modern. The term itself in its scientific sense is no older than Herbert Spencer. Animals and plants are formed as pieces of living material split from the body of the parent organisms. Their powers and faculties are fixed in their physiological origin. They are the consequence of a genetic process, and yet it is only lately that this genetic process has become the subject of systematic research and experiment. The curiosity of naturalists has of course always been attracted to such problems; but that accurate

knowledge of genetics is of paramount importance in any attempt to understand the nature of living things has only been realised quite lately even by naturalists, and with casual exceptions the laity still know nothing of the matter. Historians debate the past of the human species, and statesmen order its present or profess to guide its future as if the animal Man, the unit of their calculations, with his vast diversity of powers, were a homogeneous material, which can be multiplied like shot.

The reason for this neglect lies in ignorance and misunderstanding of the nature of Variation; for not until the fact of congenital diversity is grasped, with all that it imports, does knowledge of the system of hereditary transmission stand out as a primary necessity in the construction of any theory of Evolution, or any scheme of human polity.

The first full perception of the significance of variation we owe to Darwin. The present generation of evolutionists realises perhaps more fully than did the scientific world in the last century that the theory of Evolution had occupied the thoughts of many and found acceptance with not a few before ever the "Origin" appeared. We have come also to the conviction that the principle of Natural Selection cannot have been the chief factor in delimiting the species of animals and plants, such as we now with fuller knowledge see them actually to be. We are even more sceptical as to the validity of that appeal to changes in the conditions of life as direct causes of modification, upon which latterly at all events Darwin laid much emphasis. But that he was the first to provide a body of fact demonstrating the variability of living things; whatever be its causation, can never be questioned.

There are some older collections of evidence, chiefly the work of the French school, especially of Godron ("De l'Espèce et des Races dans les Êtres Organisés," 1859)—and I would mention also the almost forgotten essay of Wollaston ("On the Variation of Species," 1856)—these, however, are only fragments in comparison. Darwin regarded variability as a property inherent in living things, and eventually we must consider whether this conception is well founded; but postponing that inquiry for the present, we may declare that with him began a general recognition of variation as a phenomenon widely occurring in Nature.

If a population consists of members which are not alike but differentiated, how will their characteristics be distributed among their offspring? This is the problem which the modern student of heredity sets out to investigate. Formerly it was hoped that by the simple inspection of embryological processes the modes of heredity might be ascertained, the actual mechanism by which the offspring is formed from the body of the parent. In that endeavour a noble pile of evidence has been accumulated. All that can be made visible by existing methods has been seen, but we come little if at all nearer to the central mystery. We see nothing that we can analyse further—nothing that can be translated into terms less inscrutable than the physiological events themselves. Not only does embryology give no direct aid, but the failure of cytology is, so far as I can judge, equally complete. The chromosomes of nearly related creatures may be utterly different both in number, size, and form. Only one piece of evidence encourages the old hope that a connection might be traceable between the visible characteristics of the body and those of the chromosomes. I refer of course to the accessory chromosome, which in many animals distinguishes the spermatozoon about to form a female in fertilisation. Even it however cannot be claimed as the cause of sexual differentiation, for it may be paired in forms closely allied to those in which it is unpaired or accessory. The distinction may be present or wanting, like any other secondary sexual character. Indeed, so long as no one can show consistent distinctions between the cytological characters of somatic tissues in the same individual we can scarcely expect to perceive such distinctions between the chromosomes of the various types.

For these methods of attack we now substitute another, less ambitious, perhaps, because less comprehensive, but not less direct. If we cannot see how a toad by its egg and its sperm gives rise to a chicken or how a Sweet Pea from its ovule and its pollen grain produces another Sweet Pea, we at least can watch the system by which the differences between the various kinds of fowls or between the various kinds of Sweet Peas are distributed among the offspring. By thus breaking the main problem up into its parts we give ourselves fresh chances. This analytical study we call Mendelian because Mendel was the first to apply it. To be sure, he did not approach the problem by any such line of reasoning as I have sketched. His object was to determine the genetic definiteness of species; but though in his writings he makes no mention of inheritance it is clear that he had the extension in view. By cross-breeding he combined the characters of varieties in mongrel individuals and set himself to see how these characters would be distributed among the individuals of subsequent generations. Until he began this analysis nothing but the vaguest answers to such a question had been attempted. The existence of any orderly system of descent was never even suspected. In their manifold complexity human characteristics seemed to follow no obvious system, and the fact was taken as a fair sample of the working of heredity.

Misconception was especially brought in by describing descent in terms of "blood." The common speech uses expressions such as consanguinity, pure-blooded, half-blood, and the like, which call up a misleading picture to the mind. Blood is in some respects a fluid, and thus it is supposed that this fluid can be both quantitatively and qualitatively diluted with other bloods, just as treacle can be diluted with water. Blood in primitive physiology being the peculiar vehicle of life, at once its essence and its corporeal abode, these ideas of dilution and compounding of characters in the commingling of bloods inevitably suggest that the ingredients of the mixture once combined are inseparable, that they can be brought together in any relative amounts, and in short that in heredity we are concerned mainly with a quantitative problem. Truer notions of genetic physiology are given by the Hebrew expression "seed." It we speak of a man as "of the blood-royal" we think at once of plebeian dilution, and we wonder how much of the royal fluid is likely to be "in his veins"; but if we say he is "of the seed of Abraham" we feel something of the permanence and indestructibility of that germ which can be divided and scattered among all nations, but remains recognisable in type and characteristics after 4000 years.

I knew a breeder who had a chest containing bottles of coloured liquids by which he used to illustrate the relationships of his dogs, pouring from one to another and titrating them quantitatively to illustrate their pedigrees. Galton was beset by the same kind of mistake when he promulgated his "Law of Ancestral Heredity." With modern research all this has been cleared away. The allotment of characteristics among offspring is not accomplished by the exudation of drops of a tincture representing the sum of the characteristics of the parent organism, but by a process of *cell-division*, in which numbers of these characters, or rather the elements upon which they depend, are sorted out among the resulting germ-cells in an orderly fashion. What these elements, or *factors* as we call them, are we do not know. That they are in some way directly transmitted by the material of the ovum and of the spermatozoon is obvious, but it seems to me unlikely that they are in any simple or literal sense material particles. I suspect rather that their properties depend on some phenomenon of arrangement. However that may be, analytical breeding proves that it is according to the distribution of these genetic factors, to use a non-committal term, that the characters of the offspring are decided. The first business of experimental genetics is to determine their number and interactions, and then to make an analysis of the various types of life.

Now the ordinary genealogical trees, such as those which the stud-books provide in the case of the domestic animals, or the Heralds' College provides in the case of man, tell nothing of all this. Such methods of depicting descent cannot even show the one thing they are devised to show—purity of "blood." For at last we know the physiological meaning of that expression. An organism is pure-bred when it has been formed by the union in fertilisation of two germ-cells which are alike in the factors they bear; and since the factors for the several characteristics are independent of each other, this question of purity must be separately considered for each of them. A man, for example, may be pure-bred in respect of his musical ability and cross-bred in respect of the colour of his eyes or the shape of his mouth. Though we know nothing of the essential nature of these factors, we know a good deal of their powers. They may confer height, colour, shape, instincts, powers both of mind and body; indeed, so many of the attributes which animals and plants possess that we feel justified in the expectation that with continued analysis they will be proved to be responsible for most if not all of the differences by which the varying individuals of any species are distinguished from each other. I will not assert that the greater differences which characterise distinct Species are due generally to such independent factors, but that is the conclusion to which the available evidence points. All this is now so well understood, and has been so often demonstrated and expounded, that details of evidence are now superfluous.

But for the benefit of those who are unfamiliar with such work let me briefly epitomise its main features and consequences. Since genetic factors are definite things, either present in or absent from any germ-cell, the individual may be either "pure-bred" for any particular factor, or its absence, if he is constituted by the union of two germ-cells both possessing or both destitute of that factor. If the individual is thus pure, all his germ-cells will in that respect be identical, for they are simply bits of the similar germ-cells which united in fertilisation to produce the parent organism. We thus reach the essential principle, that an organism cannot pass on to offspring a factor which it did not itself receive in fertilisation. Parents, therefore, which are both destitute of a given factor can only produce offspring equally destitute of it; and, on the contrary, parents both pure-bred for the presence of a factor produce offspring equally pure-bred for its presence. Whereas the germ-cells of the pure-bred are all alike, those of the cross-bred, which results from the union of dissimilar germ-cells, are mixed in character. Each positive factor segregates from its negative opposite, so that some germ-cells carry the factor and some do not. Once the factors have been identified by their effects, the average composition of the several kinds of families formed from the various matings can be predicted.

Only those who have themselves witnessed the fixed operations of these simple rules can feel their full significance. We come to look behind the simulacrum of the individual body and we endeavour to disintegrate its features into the genetic elements by whose union the body was formed. Set out in cold general phrases such discoveries may seem remote from ordinary life. Become familiar with them and you will find your outlook on the world has changed. Watch the effects of segregation among the living things with which you have to do—plants, fowls, dogs, horses, that mixed concourse of humanity we call the English race, your friends' children, your own children, yourself—and however firmly imagination be restrained to the bounds of the known and the proved, you will feel something of that range of insight into Nature which Mendelism has begun to give. The question is often asked whether there are not also in operation systems of descent quite other than those contemplated by the Mendelian rules. I myself have expected such discoveries, but hitherto none have been plainly demonstrated. It is true we are often puzzled by the failure of a parental type to reappear in its completeness

after a cross—the merino sheep or the fantail pigeon, for example. These exceptions may still be plausibly ascribed to the interference of a multitude of factors, a suggestion not easy to disprove; though it seems to me equally likely that segregation has been in reality imperfect. Of the descent of quantitative characters we still know practically nothing. These and hosts of difficult cases remain almost untouched. In particular the discovery of E. Baur, and the evidence of Winkler in regard to his "graft hybrids," both showing that the sub-epidermal layer of a plant—the layer from which the germ-cells are derived—may bear exclusively the characters of a part only of the soma, give hints of curious complications, and suggest that in plants at least the interrelations between soma and gamete may be far less simple than we have supposed. Nevertheless, speaking generally, we see nothing to indicate that qualitative characters descend, whether in plants or animals, according to systems which are incapable of factorial representation.

The body of evidence accumulated by this method of analysis is now very large, and is still growing fast by the labours of many workers. Progress is also beginning along many novel and curious lines. The details are too technical for inclusion here. Suffice it to say that not only have we proof that segregation affects a vast range of characteristics, but in the course of our analysis phenomena of most unexpected kinds have been encountered. Some of these things twenty years ago must have seemed inconceivable. For example, the two sets of sex organs, male and female, of the same plant may not be carrying the same characteristics; in some animals characteristics, quite independent of sex, may be distributed solely or predominantly to one sex; in certain species the male may be breeding true to its own type, while the female is permanently mongrel, throwing off eggs of a distinct variety in addition to those of its own type; characteristics, essentially independent, may be associated in special combinations which are largely retained in the next generation, so that among the grandchildren there is numerical preponderance of those combinations which existed in the grandparents—a discovery which introduces us to a new phenomenon of polarity in the organism.

We are accustomed to the fact that the fertilised egg has a polarity, a front and hind end for example; but we have now to recognise that it, or the primitive germinal cells formed from it, may have another polarity shown in the groupings of the parental elements. I am entirely sceptical as to the occurrence of segregation solely in the maturation of the germ-cells,* preferring at present to regard it as a special case of that patch-work condition we see in so many plants. These mosaics may break up, emitting bud-sports at various cell-divisions, and I suspect that the great regularity seen in the F_2 ratios of the cereals, for example, is a consequence of very late segregation, whereas the excessive irregularity found in other cases may be taken to indicate that segregation can happen at earlier stages of differentiation.

The paradoxical descent of colour-blindness and other sex-limited conditions—formerly regarded as an inscrutable caprice of nature—has been represented with approximate correctness, and we already know something as to the way, or, perhaps, I should say ways, in which the determination of sex is accomplished in some of the forms of life—though, I hasten to add, we have no inkling as to any method by which that determination may be influenced or directed. It is obvious that such discoveries have bearings on most of the problems, whether theoretical or practical, in which animals and plants are concerned. Permanence or change of type, perfection of type, purity or mixture of race, "racial development," the succession of forms, from being vague phrases expressing matters of degree, are now seen to be capable of acquiring physio-

logical meanings, already to some extent assigned with precision. For the naturalist—and it is to him that I am especially addressing myself to-day—these things are chiefly significant as relating to the history of organic beings—the theory of Evolution, to use our modern name. They have, as I shall endeavour to show in my second Address to be given in Sydney, an immediate reference to the conduct of human society.

I suppose that everyone is familiar in outline with the theory of the Origin of Species which Darwin promulgated. Through the last fifty years this theme of the Natural Selection of favoured races has been developed and expounded in writings innumerable. Favoured races certainly can replace others. The argument is sound, but we are doubtful of its value. For us that debate stands adjourned. We go to Darwin for his incomparable collection of facts. We would fain emulate his scholarship, his width, and his power of exposition, but to us he speaks no more with philosophical authority. We read his scheme of Evolution as we would those of Lucretius or of Lamarck, delighting in their simplicity and their courage. The practical and experimental study of Variation and Heredity has not merely opened a new field; it has given a new point of view and new standards of criticism. Naturalists may still be found expounding teleologica systems* which would have delighted Dr. Pangloss himself, but at the present time few are misled. The student of genetics knows that the time for the development of theory is not yet. He would rather stick to the seed-pan and the incubator.

In face of what we now know of the distribution of variability in nature the scope claimed for Natural Selection in determining the fixity of Species must be greatly reduced. The doctrine of the survival of the fittest is undeniable so long as it is applied to the organism as a whole, but to attempt by this principle to find value in all definiteness of parts and functions, and in the name of Science to see fitness everywhere is mere eighteenth-century optimism. Yet it was in application to the parts, to the details of specific difference, to the spots on the peacock's tail, to the colouring of an Orchid flower, and hosts of such examples, that the potency of Natural Selection was urged with the strongest emphasis. Shorn of these pretensions the doctrine of the survival of favoured races is a truism, helping scarcely at all to account for the diversity of species. Tolerance plays almost as considerable a part. By these admissions almost the last shred of that teleological fustian with which Victorian philosophy loved to clothe the theory of Evolution is destroyed. Those who would proclaim that whatever is right will be wise henceforth to base this faith frankly on the impregnable rock of superstition, and to abstain from direct appeals to natural fact.

My predecessor said last year that in physics the age is one of rapid progress and profound scepticism. In at least as high a degree this is true of Biology, and as a chief characteristic of modern evolutionary thought we must confess also to a deep but irksome humility in presence of great vital problems. Every theory of Evolution must be such as to accord with the facts of physics and chemistry, a primary necessity to which our predecessors paid small heed. For them the unknown was a rich mine

* I take the following from the Abstract of a recent Croonian Lecture, "On the Origin of Mammals," delivered to the Royal Society:—"In Upper Triassic times the larger Cynodonts predated upon the large Anomodont. *Kannemeyria*, and carried on their existence so long as these Anomodonts survived, but died out with them about the end of the Trias or in Rhaetic times. The small Cynodonts, having neither small Anomodonts nor small Cynodonts to feed on, were forced to hunt the very active long-limbed Thecodonts. The greatly increased activity brought about that series of changes which formed the mammals—the flexible skin with hair, the four-chambered heart and warm blood, the loose jaw with teeth for mastication, an increased development of tactile sensation, and a great increase of cerebrum. Not improbably the attacks of the newly-evolved Cynodont or mammalian type brought about a corresponding evolution in the Pseudosuchia Thecodonts which ultimately resulted in the formation of Dinosaurs and Birds" (R. Broom, *Proc. Roy. Soc.*, B, lxxvii., 88).

* The fact that in certain plants the male and female organs respectively carry distinct factors may be quoted as almost decisively negating the suggestion that segregation is confined to the reduction division.

of possibilities on which they could freely draw. For us it is rather an impenetrable mountain out of which the truth can be chipped in rare and isolated fragments. Of the physics and chemistry of life we know next to nothing. Somehow the characters of living things are bound up in properties of colloids, and are largely determined by the chemical powers of enzymes, but the study of these classes of matter have only just begun. Living things are found by a simple experiment to have powers undreamt of, and who knows what may be behind?

Naturally we turn aside from generalities. It is no time to discuss the origin of the Mollusca or of Dicotyledons, while we are not even sure how it came to pass that *Primula obconica* has in twenty-five years produced its abundant new forms almost under our eyes. Knowledge of heredity has so reacted on our conceptions of variation that very competent men are even denying that variation in the old sense is a genuine occurrence at all. Variation is postulated as the basis of all evolutionary change. Do we then as a matter of fact find in the world about us variations occurring of such a kind as to warrant faith in a contemporary progressive Evolution? Till lately most of us would have said "yes" without misgiving. We should have pointed, as Darwin did, to the immense range of diversity seen in many wild species, so commonly that the difficulty is to define the types themselves. Still more conclusive seemed the profusion of forms in the various domesticated animals and plants, most of them incapable of existing even for a generation in the wild state, and therefore fixed unquestionably by human selection. These, at least, for certain, are new forms, often distinct enough to pass for species, which have arisen by variation. But when analysis is applied to this mass of variation the matter wears a different aspect. Closely examined, what is the "variability" of wild species? What is the natural fact which is denoted by the statement that a given species exhibits much variation? Generally one of two things: either that the individuals collected in one locality differ among themselves; or, perhaps, more often that samples from separate localities differ from each other. As direct evidence of variation it is clearly to the first of these phenomena that we must have recourse—the heterogeneity of a population breeding together in one area. This heterogeneity may be in any degree, ranging from slight differences that systematists would disregard, to a complex variability such as we find in some moths where there is an abundance of varieties so distinct that many would be classified as specific forms but for the fact that all are freely breeding together. Naturalists formerly supposed that any of these varieties might be bred from any of the others. Just as the reader of novels is prepared to find that any kind of parents might have any kind of children in the course of the story, so was the evolutionist ready to believe that any pair of moths might produce any of the varieties included in the species. Genetic analysis has disposed of all these mistakes. We have no longer the smallest doubt that in all these examples the varieties stand in a regular descending order, and that they are simply terms in a series of combinations of factors separately transmitted, of which each may be present or absent.

The appearance of contemporary variability proves to be an illusion. Variation from step to step in the series must occur either by the addition or by the loss of a factor. Now, of the origin of new forms by loss there seems to me to be fairly clear evidence, but of the contemporary acquisition of any new factor I see no satisfactory proof, though I admit there are rare examples which may be so interpreted. We are left with a picture of variation utterly different from that which we saw at first. Variation now stands out as a definite physiological event. We have done with the notion that Darwin came latterly to favour, that large differences can arise by accumulation of small differences. Such small differences are often mere ephemeral effects of conditions of life, and as such are not transmissible; but even small differences, when truly

genetic, are factorial like the larger ones, and there is not the slightest reason for supposing that they are capable of summation. As to the origin or source of these positive separable factors, we are without any indication or surmise. By their effects we know them to be definite, as definite, say, as the organisms which produce diseases; but how they arise and how they come to take part in the composition of the living creature so that when present they are treated in cell-division as constituent of the germs, we cannot conjecture.

It was a commonplace of evolutionary theory that at least the domestic animals have been developed from a few wild types. Their origin was supposed to present no difficulty. The various races of fowl, for instance, all came from *Gallus bankiva*, the Indian jungle fowl. So we are taught; but try to reconstruct the steps in their evolution, and you realise your hopeless ignorance. To be sure there are breeds, such as Black-red Game and Brown Leghorns, which have the colours of the jungle-fowl, though they differ in shape and other respects. As we know so little as yet of the genetics of shape, let us assume that those transitions could be got over. Suppose, further, as is probable, that the absence of the maternal instinct in the Leghorn is due to loss of one factor which the jungle-fowl possesses. So far, we are on fairly safe ground. But how about White Leghorns? Their origin may seem easy to imagine, since white varieties have often arisen in well-authenticated cases. But the white of White Leghorns is not, as white in nature often is, due to the loss of the colour-elements, but to the action of something which inhibits their expression. Whence did that something come? The same question may be asked respecting the heavy breeds, such as Malays or Indian Game. Each of these is a separate introduction from the East. To suppose that these, with their peculiar combs and close feathering, could have been developed from pre-existing European breeds is very difficult. On the other hand, there is no wild species now living any more like them. We may, of course, postulate that there was once such a species, now lost. That is quite conceivable, though the suggestion is purely speculative. I might thus go through the list of domesticated animals and plants of ancient origin and again and again we should be driven to this suggestion, that many of their distinctive characters must have been derived from some wild original now lost. Indeed, to this unsatisfying conclusion almost every careful writer on such subjects is now reduced. If we turn to modern evidence the case looks even worse. The new breeds of domestic animals made in recent times are the carefully selected products of recombination of pre-existing breeds. Most of the new varieties of cultivated plants are the outcome of deliberate crossing. There is generally no doubt in the matter. We have pretty full histories of these crosses in *Gladiolus*, *Orchids*, *Cineraria*, *Begonia*, *Calceolaria*, *Pelargonium*, &c. A very few certainly arise from a single origin. The Sweet Pea is the clearest case, and there are others which I should name with hesitation. The Cyclamen is one of them, but we know that efforts to cross Cyclamens were made early in the cultural history of the plant, and they may very well have been successful. Several plants for which single origins are alleged, such as the Chinese Primrose, the Dahlia, and Tobacco, came to us in an already domesticated state, and their origins remain altogether mysterious. Formerly single origins were generally presumed, but at the present time numbers of the chief products of domestication, dogs, horses, cattle, sheep, poultry, wheat, oats, rice, plums, cherries, have in turn been accepted as "polyphyletic," or, in other words, derived from several distinct forms. The reason that has led to these judgments is that the distinctions between the chief varieties can be traced as far back as the evidence reaches, and that these distinctions are so great, so far transcending anything that we actually know variation capable of effecting, that it seems pleasanter to postpone the difficulty, relegating the critical differentia-

tion to some misty antiquity into which we shall not be asked to penetrate. For it need scarcely be said that this is mere procrastination. If the origin of a form under domestication is hard to imagine, it becomes no easier to conceive of such enormous deviations from type coming to pass in the wild state. Examine any two thoroughly distinct species which meet each other in their distribution, as, for instance, *Lychnis diurna* and *vespertina* do. In areas of overlap are many intermediate forms. These used to be taken to be transitional steps, and the specific distinctness of *vespertina* and *diurna* was on that account questioned. Once it is known that these supposed intergrades are merely mongrels between the two species the transition from one to the other is practically beyond our powers of imagination to conceive. If both these can survive, why has their common parent perished? Why when they cross do they not reconstruct it instead of producing partially sterile hybrids? I take this example to show how entirely the facts were formerly misinterpreted.

When once the idea of a true breeding—or, as we may say, homozygous—type is grasped, the problem of variation becomes an insistent oppression. What can make such a type vary? We know, of course, one way by which novelty can be introduced—by crossing. Cross two well-marked varieties—for instance, of Chinese Primula—each breeding true, and in the second generation by mere recombination of the various factors which the two parental types severally introduced, there will be a profusion of forms, utterly unlike each other, distinct also from the original parents. Many of these can be bred true, and if found wild would certainly be described as good species. Confronted by the difficulty I have put before you, and contemplating such amazing polymorphism in the second generation from a cross in *Antirrhinum*, Lotsy has lately with great courage suggested to us that all variation may be due to such crossing. I do not disguise my sympathy with this effort. After the blind complacency of conventional evolutionists it is refreshing to meet so frank an acknowledgment of the hardness of the problem. Lotsy's utterance will at least do something to expose the artificiality of systematic zoology and botany. Whatever might or might not be revealed by experimental breeding, it is certain that without such tests we are merely guessing when we profess to distinguish specific limits, and to declare that this is a species and that a variety. The only definable unit in classification is the homozygous form which breeds true. When we presume to say that such and such differences are trivial and such others valid, we are commonly embarking on a course for which there is no physiological warrant. Who could have foreseen that the Apple and the Pear—so like each other that their botanical differences are evasive—could not be crossed together, though species of *Antirrhinum* so totally unlike each other as *majus* and *molle* can be hybridised, as Baur has shown, without a sign of impaired fertility? Jordan was perfectly right. The true-breeding forms which he distinguished in such multitudes are real entities, though the great systematists, dispensing with such laborious analysis, have pooled them into arbitrary Linnean species, for the convenience of collectors and for the simplification of catalogues. Such pragmatical considerations may mean much in the museum, but with them the student of the physiology of variation has nothing to do. These "little species," finely cut, true breeding, and innumerable mongrels between them, are what he finds when he examines any so-called variable type. On analysis the semblance of variability disappears, and the illusion is shown to be due to segregation and recombination of series of factors on pre-determined lines. As soon as the "little species" are separated out they are found to be fixed. In face of such a result we may well ask with Lotsy is there such a thing as spontaneous variation anywhere? His answer is that there is not.

Abandoning the attempt to show that positive factors can be added to the original stock, we have further to confess that we cannot often actually prove variation by

loss of factor to be a real phenomenon. Lotsy doubts whether even this phenomenon occurs. The sole source of variation, in his view, is crossing. But here I think he is on unsafe ground. When a well-established variety like "Crimson King" Primula, bred by Messrs. Sutton in thousands of individuals, gives off, as it did a few years since, a salmon-coloured variety, "Coral King," we might claim this as a genuine example of variation by loss. The new variety is a simple recessive. It differs from "Crimson King" only in one respect, the loss of a single colour-factor, and, of course, bred true from its origin. To account for the appearance of such a new form by any process of crossing is exceedingly difficult. From the nature of the case there can have been no cross since "Crimson King" was established, and hence the salmon must have been concealed as a recessive from the first origin of that variety, even when it was represented by very few individuals, probably only by a single one. Surely, if any of these had been heterozygous for salmon this recessive could hardly have failed to appear during the process of self-fertilisation by which the stock would be multiplied, even though that selfing may not have been strictly carried out. Examples like this seem to me practically conclusive.* They can be challenged, but not, I think, successfully. Then, again, in regard to those variations in number and division of parts which we call meristic, the reference of these to original cross-breeding is surely barred by the circumstances in which they often occur. There remain also the rare examples mentioned already in which a single wild origin may with much confidence be assumed. In spite of repeated trials, no one has yet succeeded in crossing the Sweet Pea with any other leguminous species. We know that early in its cultivated history it produced at least two marked varieties which I can only conceive of as spontaneously arising, though, no doubt, the profusion of forms we now have was made by the crossing of those original varieties. I mention the Sweet Pea thus prominently for another reason, that it introduces us to another though subsidiary form of variation, which may be described as a *fractionation* of factors. Some of my Mendelian colleagues have spoken of genetic factors as permanent and indestructible. Relative permanence in a sense they have, for they commonly come out unchanged after segregation. But I am satisfied that they may occasionally undergo a quantitative disintegration, with the consequence that varieties are produced intermediate between the integral varieties from which they were derived. These disintegrated conditions I have spoken of as subtraction—or reduction—stages. For example, the Picotee Sweet Pea, with its purple edges, can surely be nothing but a condition produced by the factor which ordinarily makes the fully purple flower, quantitatively diminished. The pied animal, such as the Dutch rabbit, must similarly be regarded as the result of partial defect of the chromogen from which the pigment is formed, or conceivably of the factor which effects its oxidation. On such lines I think we may with great confidence interpret all those intergrading forms which breed true and are not produced by factorial interference.

It is to be inferred that these fractional degradations are the consequence of irregularities in segregation. We constantly see irregularities in the ordinary meristic processes, and in the distribution of somatic differentiation. We are familiar with half segments, with imperfect twinning, with leaves partially petaloid, with petals partially sepaloid. All these are evidences of departures from the normal regularity in the rhythms of repetition, or in those waves of differentiation by which the qualities are sorted out among the parts of the body. Similarly, when in segregation the qualities are sorted out among the germ-cells in certain critical cell-divisions, we cannot expect these differentiating divisions to be exempt from the imperfections and irregularities which are found in all the grosser divi-

* The numerous and most interesting "mutations" recorded by Professor T. H. Morgan and his colleagues in the fly, *Drosophila*, may also be cited as unexceptionable cases.

sions that we can observe. If I am right, we shall find evidence of these irregularities in the association of unconformable numbers with the appearance of the novelties which I have called fractional. In passing let us note how the history of the Sweet Pea belies those ideas of a continuous evolution with which we had formerly to contend. The big varieties came first. The little ones have arisen later, as I suggest by fractionation. Presented with a collection of modern Sweet Peas how prettily would the devotees of Continuity have arranged them in a graduated series, showing how every intergrade could be found, passing from the full colour of the wild Sicilian species in one direction to white, in the other to the deep purple of "Black Prince," though happily we know these two to be among the earliest to have appeared.

Having in view these and other considerations which might be developed, I feel no reasonable doubt that though we may have to forego a claim to variations by addition of factors, yet variation both by loss of factors and by fractionation of factors is a genuine phenomenon of contemporary nature. If then we have to dispense, as seems likely, with any addition from without we must begin seriously to consider whether the course of Evolution can at all reasonably be represented as an unpacking of an original complex which contained within itself the whole range of diversity which living things present. I do not suggest that we should come to a judgment as to what is or is not probable in these respects. As I have said already, this is no time for devising theories of Evolution, and I propound none. But as we have got to recognise that there has been an Evolution, that somehow or other the forms of life have arisen from fewer forms, we may as well see whether we are limited to the old view that evolutionary progress is from the simple to the complex, and whether after all it is conceivable that the process was the other way about. When the facts of genetic discovery become familiarly known to biologists, and cease to be the preoccupation of a few, as they still are, many and long discussions must inevitably arise on the question, and I offer these remarks to prepare the ground. I ask you simply to open your minds to this possibility. It involves a certain effort. We have to reverse our habitual modes of thought. At first it may seem rank absurdity to suppose that the primordial form or forms of protoplasm could have contained complexity enough to produce the diverse types of life. But is it easier to imagine that these powers could have been conveyed by extrinsic additions? Of what nature could these additions be? Additions of material cannot surely be in question. We are told that salts of iron in the soil may turn a pink hydrangea blue. The iron cannot be passed on to the next generation. How can the iron multiply itself? The power to assimilate the iron is all that can be transmitted. A disease-producing organism like the pebrine of silkworms can in a very few cases be passed on through the germ-cells. Such an organism can multiply and can produce its characteristic effects in the next generation. But it does not become part of the invaded host, and we cannot conceive it taking part in the geometrically ordered processes of segregation. These illustrations may seem too gross; but what refinement will meet the requirements of the problem, that the thing introduced must be, as the living organism itself is, capable of multiplication and of subordinating itself in a definite system of segregation? That which is conferred in variation must rather itself be a change, not of material, but of arrangement, or of motion. The invocation of additions extrinsic to the organism does not seriously help us to imagine how the power to change can be conferred, and if it proves that hope in that direction must be abandoned, I think we lose very little. By the re-arrangement of a very moderate number of things we soon reach a number of possibilities practically infinite.

That primordial life may have been of small dimensions need not disturb us. Quantity is of no account in these considerations. Shakespeare once existed as a speck of protoplasm not so big as a small pin's head. To this

nothing was added that would not equally well have served to build up a baboon or a rat. Let us consider how far we can get by the process of removal of what we call "epistatic" factors, in other words those that control, mask, or suppress underlying powers and faculties. I have spoken of the vast range of colours exhibited by modern Sweet Peas. There is no question that these have been derived from the one wild bi-colour form by a process of successive removals. When the vast range of form, size, and flavour to be found among the cultivated apples is considered it seems difficult to suppose that all this variety is hidden in the wild crab-apple. I cannot positively assert that this is so, but I think all familiar with Mendelian analysis would agree with me that it is probable, and that the wild crab contains presumably inhibiting elements which the cultivated kinds have lost. The legends that the seedlings of cultivated apples become crabs is often repeated. After many inquiries among the raisers of apple seedlings I have never found an authentic case—once only even an alleged case, and this on inquiry proved to be unfounded. I have confidence that the artistic gifts of mankind will prove to be due not to something added to the make-up of an ordinary man, but to the absence of factors which in the normal person inhibit the development of these gifts. They are almost beyond doubt to be looked upon as releases of powers normally suppressed. The instrument is there, but it is "stopped down." The scents of flowers or fruits, the finely repeated divisions that give its quality to the wool of the Merino, or in an analogous case the multiplicity of quills to the tail of the fantail pigeon, are in all probability other examples of such releases. You may ask what guides us in the discrimination of the positive factors and how we can satisfy ourselves that the appearance of a quality is due to loss. It must be conceded that in these determinations we have as yet recourse only to the effects of dominance. When the tall pea is crossed with the dwarf, since the offspring is tall we say that the tall parent passed a factor into the cross-bred which makes it tall. The pure tall parent had two doses of this factor; the dwarf had none; and since the cross-bred is tall we say that one dose of the dominant tallness is enough to give the full height. The reasoning seems unanswerable. But the commoner result of crossing is the production of a form intermediate between the two pure parental types. In such examples we see clearly enough that the full parental characteristics can only appear when they are homozygous—formed from similar germ-cells, and that one dose is insufficient to produce either effect fully. When this is so we can never be sure which side is positive and which negative. Since, then, when dominance is incomplete we find ourselves in this difficulty, we perceive that the amount of the effect is our only criterion in distinguishing the positive from the negative, and when we return even to the example of the tall and dwarf peas the matter is not so certain as it seemed. Professor Cockerell lately found among thousands of yellow sunflowers one which was partly red. By breeding he raised from this a form wholly red. Evidently the yellow and the wholly red are the pure forms, and the partially red is the heterozygote. We may then say that the yellow is YY with two doses of a positive factor which inhibits the development of pigment; the red is yy, with no dose of the inhibitor; and the partially red are Yy, with only one dose of it. But we might be tempted to think the red was a positive characteristic, and invert the expressions, representing the red as RR, the partly red as Rr, and the yellow as rr. According as we adopt the one or the other system of expression we shall interpret the evolutionary change as one of loss or as one of addition. May we not interpret the other apparent new dominants in the same way? The white dominant in the fowl or in the Chinese Primula can inhibit colour. But may it not be that the original coloured fowl or Primula had two doses of a factor which inhibited this inhibitor? The Pepper Moth, *Amphidasya betularia*, produced in England about 1840 a black variety, then a novelty, now common in certain

areas, which behaves as a full dominant. The pure blacks are no blacker than the cross-bred. Though at first sight it seems that the black *must* have been something added, we can without absurdity suggest that the normal is the term in which two doses of inhibitor are present, and that in the absence of one of them the black appears.

In spite of seeming perversity, therefore, we have to admit that there is no evolutionary change which in the present state of our knowledge we can positively declare to be not due to loss. When this has been conceded it is natural to ask whether the removal of inhibiting factors may not be invoked in alleviation of the necessity which has driven students of the domestic breeds to refer their diversities to multiple origins. Something, no doubt, is to be hoped for in that direction, but not until much better and more extensive knowledge of what variation by loss may effect in the living body can we have any real assurance that this difficulty has been obviated. We should be greatly helped by some indication as to whether the origin of life has been single or multiple. Modern opinion is, perhaps, inclining to the multiple theory, but we have no real evidence. Indeed, the probable still stands outside the range of scientific investigation, and when we hear the spontaneous formation of formaldehyde mentioned as a possible first step in the origin of life, we think of Harry Lauder in the character of a Glasgow schoolboy pulling out his treasures from his pocket—"That's a wassher—for makkin' motor cars"!

As the evidence stands at present all that can be safely added in amplification of the evolutionary creed may be summed up in the statement that variation occurs as a definite event often producing a sensibly discontinuous result; that the succession of varieties comes to pass by the elevation and establishment of sporadic groups of individuals owing their origin to such isolated events; and that the change which we see as a nascent variation is often, perhaps always, one of loss. Modern research lends not the smallest encouragement or sanction to the view that gradual evolution occurs by the transformation of masses of individuals, though that fancy has fixed itself on popular imagination. The isolated events to which variation is due are evidently changes in the germinal tissues, probably in the manner in which they divide. It is likely that the occurrence of these variations is wholly irregular, and as to their causation we are absolutely without surmise or even plausible speculation. Distinct types once arisen, no doubt a profusion of the forms called species have been derived from them by simple crossing and subsequent recombination. New species may be now in course of creation by this means, but the limits of the process are obviously narrow. On the other hand, we see no changes in progress around us in the contemporary world which we can imagine likely to culminate in the evolution of forms distinct in the larger sense. By intercrossing dogs, jackals, and wolves new forms of these types can be made, some of which may be species, but I see no reason to think that from such material a fox could be bred in indefinite time, or that dogs could be bred from foxes.

Whether Science will hereafter discover that certain groups can by peculiarities in their genetic physiology be declared to have a prerogative quality justifying their recognition as species in the old sense, and that the differences of others are of such a subordinate degree that they may in contrast be termed varieties, further genetic research alone can show. I myself anticipate that such a discovery will be made, but I cannot defend the opinion with positive conviction.

Somewhat reluctantly, and rather from a sense of duty, I have devoted most of this Address to the evolutionary aspects of genetic research. We cannot keep these things out of our heads, though sometimes we wish we could. The outcome, as you will have seen, is negative, destroying much that till lately passed for gospel. Destruction may be useful, but it is a low kind of work. We are just about where Boyle was in the seventeenth century.

We can dispose of Alchemy, but we cannot make more than a quasi-chemistry. We are awaiting our Priestley and our Mendeléeff. In truth it is not these wider aspects of genetics that are at present our chief concern. They will come in their time. The great advances of science are made like those of evolution, not by imperceptible mass-improvement, but by the sporadic birth of penetrative genius. The journeymen follow after him, widening and clearing up, as we are doing along the track that Mendel found.

ADDRESS TO THE MATHEMATICAL AND PHYSICAL SCIENCE SECTION OF THE BRITISH ASSOCIATION.

AUSTRALIA, 1914.

By Prof. F. T. TROUTON, M.A., Sc.D., F.R.S.,
President of the Section.

WE have lost since the last meeting of the Section several distinguished members who have in the past added so much to the usefulness of our discussions. These include Sir Robert Ball, who was one of our oldest attendants, and was President of the Section at the Manchester Meeting in 1886; Professor Poynting, who was President of the Section at Dover in 1899; and Sir David Gill, who was President of the Association at Leicester in 1907.

It seems appropriate at this meeting in the City of Melbourne to mention one who passed away from his scientific labours somewhat previous to the last meeting. I allude to W. Sutherland of this city, whose writings have thrown so much light on Molecular Physics, and whose scientific perspicacity was only equalled by his modesty.

This meeting of the British Association will be a memorable one as being indicative, as it were, of the scientific coming of age of Australia. Not that the maturity of Australian science was unknown to those best able to judge, indeed the fact could not but be known abroad, for in England alone there are many workers in science hailing from Australia and New Zealand, who have enhanced science with their investigations, and who hold many important scientific posts in that country. In short, one finds it best nowadays to ask of any young investigator if he comes from the Antipodes.

This speaks well for the Universities and their staffs, who have so successfully set the example of scientific investigation to their pupils.

Radio-activity and kindred phenomena seem to have attracted them most of late years, and it would perhaps have been appropriate to have shortly reviewed in this Address our knowledge in these subjects, to which the sons of Australasia have so largely contributed.

Twenty-five years ago FitzGerald and others were speculating on the possibility of unlocking and utilising the internal energy of the atom. Then came the epoch-making discovery of Becquerel, to be followed by the brilliant work of Rutherford and others showing us that no key was required to unlock this energy, the door lay open.

We have still facing us the analogous case of a hitherto untapped source of energy arising from our motion through the ether. All attempts, it is true, to realise this have failed, but nevertheless he would be a brave prophet who would deny the possibility of tapping this energy despite the ingenious theories of relativity which have been put forward to explain matters away. There is no doubt but that up to the present nothing hopeful has been accomplished towards reaching this energy, and there are grave difficulties in the way; but "Relativity" is, as it were, merely trying to remove the lion in the path by laying down the general proposition that the existence of lions is an impossibility. The readiness with which the fundamental hypotheses of "Relativity" were accepted by many is characteristic of present-day Physics, or perhaps more correctly speaking is an exaggerated example of it.

Such an acceptance as this could hardly be thought of as taking place half a century ago when a purely dynamical basis was expected for the full explanation of all phenomena, and when facts were only held to be completely understood if amenable to such treatment; while, if not so, they were put temporarily into a kind of suspense account waiting the time when the phenomenon would succumb to treatment based on dynamics.

Many things, perhaps not the least among them radioactivity, have conspired to change all this, and to produce an attitude of mind prepared to be content with a much less rigid basis than would have been required by the Natural Philosophers of a past generation. These were the sturdy Protestants of Science, to use an analogy, while we of the present day are much more catholic in our scientific beliefs, and in fact it would seem that nowadays to be used to anything is synonymous with understanding it.

Leaving, however, these interesting questions, I will confine my remarks to a rather neglected corner of physics, namely, to the phenomena of Absorption and Adsorption of solutions. The term Adsorption was introduced to distinguish between Absorption which takes place throughout the mass of the absorbing material and those cases in which it takes place only over its surface. If, for instance, glass, powdered so as to provide a large surface, is introduced into a solution of a salt in water, we have, in general, some of the salt leaving the body of the solution and adhering in one form or other to the surface of the glass. It is to this the term Adsorption has been applied. Physicists have now begun to take up the question seriously, but it was to Biologists and especially Physiological Chemists that most of our knowledge of the subject in the past was due, the phenomenon being particularly attractive to them, seeing that so many of the processes they are interested in take place across surfaces.

As far as investigations already made go, the laws of Adsorption appear to be very complicated, and no doubt many of the conflicting experimental results which have been obtained are in part due to this, workers under somewhat different conditions obtaining apparently contradictory effects.

On the whole, however, it may be said that the amount adsorbed increases with the strength of solution according to a simple power law, and diminishes with rise of temperature; but there are many exceptions to these simple rules. For instance, in the case of certain sulphates and nitrates the amount adsorbed by the surface of, say, precipitated silica, only increases up to a certain critical point as the strength of the solution is increased. Then further increase in the strength of the solution causes the surface to give up some of the salt it has already adsorbed or the amount adsorbed is actually less now than that adsorbed from weaker solutions. Beyond this stage for still greater concentrations of the solutions the amount adsorbed goes on increasing as before the critical point was reached.

There is some reason for thinking that there are two modes in which the salt is taken up or adsorbed by the solid surface. The first of them results from a simple strengthening of the solution in the surface layers; the second, which takes place with rather stronger concentrations, is a deposition in what is apparently analogous to the solid form. It would seem that the first reaches out from the solid surface to about 10^{-8} cm.—which is the order of the range of attraction of the particles of the solid substance.

The cause of the diminution in the adsorption layer at a certain critical value of the concentration is difficult to understand. Something analogous has been observed by Lord Rayleigh in the thickness of layers of oil floating on the surface of water. As oil is supplied the thickness goes on increasing up to a certain point, beyond this, on further addition of oil, the layer thins itself at some places, and becomes much thicker at others, intermediate thicknesses to these being apparently unstable and unable to exist.

As helping towards an explanation of the diminution in the adsorption layer we may suppose that as the strength of the solution is increased from zero, the adsorption is at first merely an increased density of the solution in the surface layer. For some reason, after this has reached a certain limit, further addition of salt to the solution renders this mode of composition of the surface layers unstable, and there is a breaking up of the arrangement of the layer with a diminution in its amount. We may now suppose the second mode of deposition to begin to show its effect with a recovery in the amount of the surface layers, and a further building up of the adsorption deposits.

On account of passing this point of instability the process is irreversible so that the application of thermodynamics to the phenomenon of adsorption is necessarily greatly restricted in its usefulness.

A possible cause of the instability in the adsorption layer which occurs at the critical point may be looked for in the alternations in the sign of the mutual forces between attracting particles of the kind suggested by Lord Kelvin and others. Within a certain distance apart—the molecular range—the particles of matter mutually attract one another, while at very close distances they obviously must repel, for two particles refuse to occupy the same space. At some intermediate distances the force must pass through zero value. It has for various reasons been thought that, in addition, the force has zero value at a second distance lying between the first zero and the molecular range, with accompanying alternations in the sign of the force. Thus, starting from zero distance apart of the particles, the sign of the force is negative or repulsive; then, as the distance apart is supposed to increase, the force of repulsion diminishes, and after passing through zero value becomes positive or attractive; next, as the distance is increased the force diminishes again, and after passing through a second zero becomes negative for a second time; finally, the force on passing through a third zero becomes positive, and is then in the stage dealt with in capillary and other questions.

As an instance, of where these alternations of sign seem to be manifest, may be mentioned the case of certain crystals when split along cleavage planes. The split often runs along further than the position of the splitting instrument or inserted wedge seems to warrant. This would occur if the particles on either side of the cleavage plane were situated at the distance apart where the force between them was in the first attractive condition, for then on increasing the distance between the particles by means of the wedge the force changes sign and becomes repulsive, thus helping the splitting to be propagated further out.

Assuming that a repulsive force can supervene between the particles in the adsorption layer, through the particles becoming so crowded in places as to reduce their mutual distances to the stage when repulsion sets in, we might expect that an instability would be set up.

As already stated, a rise in temperature reduces in general the amount adsorbed; but below the critical point the nitrates and sulphates are exceptional, for rise in temperature here increases the amount adsorbed from a given solution. This obviously necessitates that the isothermals cross one another at the critical point in an Adsorption-Concentration diagram. This may perhaps account for some observers finding that adsorption did not change with temperature. We have another exception to the simple laws of adsorption in the case of the alkali chlorides; this exception occurs under certain conditions of temperature and strength of solution. The normal condensation into the surface layer is reversed and the salt is repelled into the general solution instead of being attracted by the surface. In other words, it is the turn of the other constituent of the solution, namely, the water, to be adsorbed.

It is a very well known experiment in adsorption to run a solution such as that of permanganate of potash through a filter of sand, or, better, one of precipitated silica, so as to provide a very large surface. The first of the solution

to come through the filter has practically lost all its salt owing to having been adsorbed by the surface of the sand.

I was interested in finding a few months ago that Defoe, the author of "Robinson Crusoe," in one of his other books, depicts a party of African travellers as being saved from thirst in a place where the water was charged with alkali by filtering the water through bags of sand. Whether this is a practical thing or not is doubtful, or even if it has ever been tried; for it is only the first part of the liquid to come through the filter which is purified, and very soon the surface has taken up all the salt it can adsorb, and after that, of course, the solution comes through intact. It is interesting, however, to know that so long ago as Defoe's time the phenomenon of adsorption from salt solutions had been observed. It is not so well known that in the case of some salts under the circumstances mentioned above, the first of the solution to come through the sand filter is stronger instead of weaker. This, as already mentioned, is because water, or at least a weaker solution, forms the adsorption layer.

Most of the alkali chlorides as the temperature is raised show this anomalous adsorption, provided the strength of the solution is below a certain critical value differing for each temperature. For strengths of solution above these values the normal phenomenon takes place.

No investigations seem to have been made on the effect of pressure on adsorption. These data are much to be desired.

The investigation of adsorption and absorption should throw light on Osmosis, as in the first place the phenomenon occurs across a surface necessarily covered with an adsorption layer, and in the second place, as we shall see, the final condition is an equilibrium between the absorption of water by the solution and that by the membrane.

The study of the conditions of absorption of water throughout the mass of the colloidal substance of which osmotic membranes are made is of much interest. Little work has been done on the subject as yet, but what little has been done is very promising.

It is convenient to call the material of which a semi-permeable membrane is made the semi-permeable medium. The ideal semi-permeable medium will not absorb any salt from the solution but only water, but such perfection is probably seldom to be met with. If a semi-permeable medium such as parchment paper be immersed in a solution, say of sugar, less water is taken up or absorbed than is the case when the immersion is in pure water. The diminution in the amount absorbed is found to increase with the strength of the solution. It is at the same time found that the absorption or release of water by the semi-permeable medium according as the solution is made weaker or stronger is accompanied by a swelling or shrinkage greater than can be accounted for by the water taken up or rejected.

The amount of water absorbed by a semi permeable medium from a solution is found by experiment to depend upon the hydrostatic pressure. If the pressure be increased the amount of water absorbed by the semi-permeable medium is increased. It is always thus possible by the application of pressure to force the semi-permeable medium to take up from a given solution as much water as it takes up from pure water at atmospheric pressure.

It is not possible for a mass of such a medium to be simultaneously in contact and in equilibrium with both pure water and with a solution all at one and the same pressure, seeing that the part of the medium in contact with the pure water would hold more water than that part in contact with the solution, and consequently diffusion would take place through the mass of the medium.

If, however, the medium be arranged so as to separate the solution and the water, and provided the medium is capable of standing the necessary strain, it is possible to increase the pressure of the solution without increasing the pressure of the water on the other side. Thus the part of the medium which is in contact with the solution is at a higher pressure than that part in contact with the pure

solvent; consequently the medium can be in equilibrium with both the solution and the solvent, for if the pressures are rightly adjusted the moisture throughout the medium is everywhere the same.

The ordinary arrangement for showing osmotic pressure is a case such as we are considering, and equilibrium throughout the membrane is only obtained when the necessary difference in pressure exists between the two sides of the membrane.

This condition would eventually be reached no matter how thick the membrane was. It is sometimes helpful to think of the membrane as being very thick. It precludes any temptation to view molecules as shooting across from one liquid to the other through some kind of 'peep-holes' in the membrane.

The advantage in a thin membrane in practice is simply that the necessary moisture is rapidly applied to the active surface, thus enabling the pressure on the side of the solution to rise quickly, but it has no effect on the ultimate equilibrium.

As far as that goes, the semi-permeable membrane or saturated medium might be infinitely thick, or, in other words, there need be no receptacle or place for holding the pure solvent outside the membrane at all. In fact, the function of the receptacle containing the pure solvent is only to keep the medium moist, and is no more or no less important than the vessel of water supplied to the gauze of the wet-bulb thermometer. It is merely to keep up the supply of water to the medium.

The real field where the phenomenon of osmosis takes place is the surface of separation between the saturated semi permeable medium and the solution. Imagine a large mass of colloidal substance saturated with water and having a cavity containing a solution. The pressure will now tend to rise in the cavity until it reaches the osmotic pressure—that is, until there is established an equilibrium of surface transfer of molecules from the solution into the medium and back from the medium into the solution.

No doubt, the phenomenon as thus described occurs often in Nature. It is just possible that the high-pressure liquid cavities, which mineralogists find in certain rock crystals, have been formed in some such manner in the midst of a mass of semi-permeable medium; the pure solvent in this case being carbon dioxide and the medium colloidal silica, which has since changed into quartz crystal.

In considering equilibrium between a saturated semi-permeable medium and a solution there seems to me to be a point which should be carefully considered before being neglected in any complete theory. That is, the adsorption layer over the surface of the semi-permeable medium. We have seen that solutions are profoundly modified in the surface layers adjoining certain solids, through concentration or otherwise of the salts in the surface layer, so that the actual equilibrium of surface transfer of water molecules is not between the unmodified solution and the semi-permeable medium but between the altered solution in the adsorption layer and the saturated medium. Actual determinations of the adsorption by colloids are much wanted, so as to be able to be quite sure of what this correction amounts to or even if it exists. It may turn out to be zero. If there is adsorption, however, it may possibly help to account for part of the unexpectedly high values of the osmotic pressure observed at high concentrations of the solution, the equilibrium being, as we have seen, between the saturated medium and a solution of greater concentration than the bulk of the liquid, namely, that of the adsorption layer. In addition, when above the critical adsorption point, there may be a deposit in the solid state. This may produce a kind of polarised equilibrium of surface transfer in which the molecules which discharge from the saturated medium remain unaltered in amount, but those which move back from the adsorption layer are reduced owing to this deposit, thus necessitating an increase in pressure for equilibrium. If either or both of these effects really exist, it would seem to require that the pres-

sure should be higher for equilibrium of the molecular surface transfer than if there were no adsorption layer and the unaltered solution were to touch the medium, but at the same time it should be remembered that there is a second surface where equilibrium must also exist—that is, the surface of separation of the adsorption layer and the solution itself. It is just possible that the two together cancel each other's action.

Quantitative determinations of absorption by solid media from solution are hard to carry out, but with a liquid medium it is not so difficult. Ether constitutes an excellent semi-permeable medium for use with sugar solution, because it takes up or dissolves only a small quantity of water and no sugar. A series of experiments using these for medium and solution has shown (1) that the absorption of water from a solution diminishes with the strength of the solution; and (2) that the absorption of water for any given strength of solution increases with the pressure. This increase with pressure is somewhat more rapid than if it were in proportion to the pressure. On the other hand, from pure water ether absorbs in excess of normal almost in proportion to the pressure. Certainly this is so up to 100 atmospheres. This would go to confirm the suggestion already made that the departure from proportionality in the osmotic pressure is attributable to adsorption.

By applying pressure ether can be thus made to take up the same quantity of water from any given solution as it takes up from pure water at atmospheric pressure. It is found by experiment that this pressure is the osmotic pressure proper to the solution in question.

Decidedly the most interesting fact connected with the whole question of osmotic pressure, the behaviour of vapour pressures from solution, and the equilibrium of molecular transfer of solutions with colloids, is that discovered by van 't Hoff, that the hydrostatic pressure in question is equal to what would be produced by a gas having the same number of particles as those of the introduced salt. Take the case of a mass of colloid or semi-permeable medium placed in a vessel of water; the colloid when in equilibrium at atmospheric pressure holds what we will call the normal moisture. By increasing the pressure this moisture can be increased to any desired amount. Now, on introducing salt the moisture in the colloid can be reduced at will. The question is, what quantity of salt must be introduced just to bring back the amount of the moisture in the colloid to normal? Here we get a great insight into the internal mechanism of the liquid state. The quantity of salt required turns out to be, approximately at least, that amount which if in the gaseous state would produce the pressure. So that normality can be either directly restored by removing the pressure or indirectly by introducing salt in quantity which just takes up the applied pressure. That this is so naturally suggested that the salt, although compelled to remain within the confines of the liquid, nevertheless produces the same molecular bombardment as it would were it in the gaseous state, though of course the free path must be viewed as enormously restricted compared with that in the gaseous state.

Many have felt a difficulty in accepting this view of a molecular bombardment occurring in the liquid state, but of recent years much light has been thrown on the subject of molecular movements in liquids, especially by Perrin's work, so that much of the basis of this difficulty may be fairly considered as now removed.

Quite analogous to the reduction from the normal of the moisture held by a semi-permeable medium brought about by the addition of salt to the water, is the reduction in the vapour pressure arising from the presence of a salt in the water. The vapour pressure is likewise increased by the application of hydrostatic pressure, which may be effected by means of an inert gas. In both cases the hydrostatic pressure which must be applied to bring back to normality is equal to that which the added salt would exert if it were in the state of vapour or, in other words, the osmotic pressure.

The two cases are really very similar. In both there is equal molecular transfer backwards and forwards across the bounding surface. In the one a transfer from that solution to the semi-permeable medium and back from it into the solution. In the other a transfer from the solution into the superambient vapour and back from it into the solution.

The processes are very similar, namely, equal molecular transfer to and fro across the respective surfaces of separation.

Thus we may in the case of osmotic equilibrium attribute the phenomenon with Callendar to evaporation, but not evaporation in its restricted sense, from a free surface of liquid, but as we have seen from a saturated colloidal surface into the solution. This process might perhaps be better referred to as molecular emigration, the term migration being already a familiar one in connection with liquid phenomena.

THE DIFFERENCES IN THE ATOMIC WEIGHTS OF LEAD OBTAINED FROM DIFFERENT MINERALS.

By MAURICE CURIE.

THE theory of radio-active transformations applied to the study of the families of radio-elements has enabled us to prophesy that in all these families the atomic weights of the last terms will be about 207. Some time ago Boltwood suggested the hypothesis that lead is the final term of the transformation of radium. Also the study of the mechanism of the transformations led Soddy and Fajans to assign to each radio-element a definite place in the periodic system of classification; in the two last rows of this system the radio-elements are classed in groups, the same place being occupied by several elements the atomic weights of which may differ by some units, while their chemical and electro-chemical properties appear identical.

In particular, it appears that each of the uranium, radium, thorium, actinium families ends in inactive elements which occupy the same place as lead, but have slightly different atomic weights. It would be foretold that lead coming from thorium would have a slightly higher atomic weight than ordinary lead (obtained from galena); that of lead coming from uranium would on the contrary be lower, the difference in each case being possibly about one unit. Thus ordinary lead could be regarded either as a mixture of the two others or as a different kind. It is obviously very important to prove experimentally that such differences actually exist; the theoretical forecasts relating to the classification and transformation of the radio-elements would be confirmed; moreover it would be possible to extend these conclusions to inactive elements other than lead, some of which could also be regarded as mixtures of several substances of very nearly the same atomic weights and almost identical chemical properties.

In the research which I have been carrying on for a year I proposed to compare the atomic weights of lead extracted from different minerals. After a communication on the same subject which Hönigschmidt has just addressed to the Société de Chimie Physique I have decided to publish the results obtained, although the work is not quite finished.

I tried to compare the lead of uranium minerals free from thorium with that of thorium minerals free from uranium. I used pitchblende, carnotite, yttrio-tantalite containing uranium and negligible quantities of thorium, monazite containing thorium and relatively very little uranium, and finally galena, which contained neither uranium nor thorium.

Purification.—The raw insoluble carbonates obtained from the mineral are subjected to fusion with potassium cyanide in order to eliminate the excess of alkaline earth. The melt obtained is dissolved in nitric acid, and the following series of operations is carried out:—

- i. Precipitation of lead sulphate.
- ii. Transformation of the sulphate into carbonate by ammonium carbonate, then into nitrate; in the solution the copper and silver are precipitated by laminæ of pure lead.
- iii. Re-precipitation of the sulphate.
- iv. Electrolysis of the nitrate obtained from this last sulphate.
- v. The oxide thus obtained is transformed into nitrate (reduced with cyanide and attacked by nitric acid). This nitrate is transformed into basic nitrate by partial calcination in a quartz capsule, and taken up with water; the calcination must be fairly prolonged, so that there is always an excess of insoluble oxide which is separated by filtration. The basic nitrate is transformed into neutral nitrate by the addition of nitric acid, and then the transformation into basic nitrate is effected a second time.
- vi. The neutral nitrate is again obtained and twice crystallised by the difference of solubility when heated and in the cold.
- vii. Finally lead carbonate is precipitated by ammonium carbonate; it is reduced with cyanide, the melt obtained is again fused with cyanide.

It is much more difficult to obtain a perfectly pure lead starting from radio-active minerals than from galena, in consequence of the very great complexity of these minerals, especially pitchblende. Moreover there is no means of precisely controlling the presence of traces of impurities; chemical analysis obviously fails, and spectrography does not seem effectual.

The best guarantee of purity consists in finding for each of the different leads the same atomic weight after a new purification. This condition is fulfilled by the two numbers given for each mineral (except carnotite).

Method of Determining the Atomic Weight.—Five grms. of lead are weighed in a quartz vessel. It is attacked with undiluted nitric acid. On evaporation on the water-bath crystals of nitrate are thus obtained of very small dimensions. These crystals, triturated, are raised to 145–150° for two hours and then weighed. It was found that the same values were obtained after they had again been put in the oven, even for several hours.

This method was recommended by Stas. Theoretically less accurate than the chloride method, it has the advantage over it of requiring much fewer treatments of the substance. Stress is laid, moreover, upon always working in the same conditions, the relative values being of more interest in the investigation than the absolute values. The following results were obtained:—

			Mean.
Pitchblende ..	206.60	206.68	206.64
Carnotite ..	206.38	206.34	206.36
Yttrotantalite ..	206.49	206.59 206.55	206.54
Monazite ..	207.06	207.10	207.08
Galena ..	206.98	207.04	207.01

The atomic weight obtained for lead from galena agrees well with that at present adopted, while the atomic weight of lead from uranium minerals is decidedly lower and monazite gives a slightly higher number. The results, which agree in principle with the theory, must be completed and confirmed before being considered conclusive.—*Comptes Rendus*, clviii., 1676.

Syntheses by means of Sodamide. Derivatives of β -Methylcyclopentanone.—A. Haller and R. Cornubert. — β -methylcyclopentanone can be alkylated in the position next to the carbonyl by means of sodamide, and no condensation products are formed, if a methyl group is previously introduced into the α -position with regard to the ketonic function. Like tetramethylcyclopentanone, β -methyl- α,α,α' -tetramethylcyclopentanone can be transformed into an amide of a tetramethyl caproic acid when it is heated in toluene with sodamide.—*Comptes Rendus*, clviii., No. 23.

NOTICES OF BOOKS.

Livingstone College Year Book, 1914. London: Livingstone College.

THIS year-book contains some account of the very useful training in medical work given at the college. The course of study appears to be founded upon a genuinely scientific basis, and although necessarily elementary it must be a valuable aid to men who are going abroad to remote places where a little medical and surgical knowledge is often of the greatest value. A short summary of a year's progress in tropical medicine is given, and also brief notices of books which bear upon the subject and upon general hygiene.

Enzyklopädie der Technischen Chemie. ("Encyclopædia of Technical Chemistry"). Edited by Prof. Dr. FRITZ ULLMANN. Vol. I. Berlin and Vienna: Urban and Schwarzenberg, 1914. (£1 12s. net).

THE first volume of this encyclopædia contains articles on Abanone to Athylamin, giving clear accounts of the actual state of technical practice. Long and detailed main articles, to which abundant cross references are given, are a special feature, and a high level of comprehensiveness is reached. The encyclopædia, which it is hoped to complete in ten volumes, is very well and clearly printed, and although the arrangement is alphabetical a good subject index is provided.

CORRESPONDENCE.

SIR WILLIAM CROOKES AND SIR HENRY ROSCOE
 AS EDUCATIONALISTS.

To the Editor of the Chemical News.

SIR,—In his commendatory remarks at the presentation of the Medal of the Society of Chemical Industry to Sir Henry Roscoe, Dr. Messel said that some 2000 students must have received direct teaching from the illustrious Professor. Though the least worthy of these, but who, before entering Owens College as an evening student, had derived very real benefit, if differently, from the similar labours of—as he then was—Mr. William Crookes at Chester, you possibly may think an early chapter in his life of sufficient interest to allow me to recall it in your columns. So far as I know, only the scantiest reference has ever been made to it in any biographical notice.

I refer to the establishment of the Chemical Laboratory at Chester before 1857, when chemistry was less generally studied than has since been the case. Outside of London and its University with affiliated colleges, there was perhaps at that time no better laboratory in England than the one at Chester, the plan and general arrangements of which would be chiefly due to William Crookes. He had just left the College as Chemical Lecturer and Master when I entered in 1858, as a boy, the engineering and commercial school that formed part of the institution, a unique combination that has not been perpetuated, and which only the commanding personality of the Principal, the Rev. Arthur Rigg, could have obtained authority to establish.

All the arrangements for both teacher and students, and especially relating to the method of conveying instruction, were, I can testify, most convenient and complete. Nothing appeared to have been *just introduced*, everything worked so smoothly. The various acids and reagents needed for the classes were prepared by the students during a certain hour devoted to "industrial work" every day. This was a part of the time that usually in schools would be given up to play and recreation.

With Mr. Rigg no doubt originated the idea, that his Board allowed him to carry out, of having workshops in

various parts of the College, for bookbinding, carpentry, wood-carving, the forging of iron, turning, and fitting. The laboratory during that hour became a small chemical factory, and one may imagine the incalculable benefit of this work for those of us who shared in it. The apparatus then existing in the place must of necessity have been put together under the skilful direction of him who is now President of the Royal Society. What the influence of his instruction amongst the students of the training college may have been it is impossible to say, but all who came within such influence must have become better teachers at the National Schools for being able to impart—we are even only the rudiments of—chemical knowledge to their charges, at a time when one may say that the science was being "born commercially."

I have been induced to put these few facts on record chiefly by a statement implying that discoveries are developed abroad rather than in this country, not because of any shortcoming of English science, but because of the shortsightedness of the State. It certainly is of little use to the nation to implant the love of chemistry in our students if the Government bars the way of industrial progress. In the land of Black, Priestley, Cavendish, Dalton, and so many others like them, there will never lack men of genius ready to lead into new realms of chemical knowledge; but let not the Legislature stifle those who with their industry and capital are ready to follow and work the mines of wealth thus opened out for the general benefit.—I am, &c.,

F. J. R. CARULLA.

Derby, July 21, 1914.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 23, June 8, 1914.

Diagnosis of Primary, Secondary, and Tertiary Bases.—Charles Moureu and Georges Mignonnac.—Primary and secondary bases react with ethyl magnesium bromide to give a molecule of ethane for each primary or secondary base function, while tertiary bases do not liberate the gas. Thus this reaction can be used to distinguish primary or secondary from tertiary bases. This reaction can be used for bases containing several atoms of nitrogen. The method is very rapid, and only small quantities of substance are required for it. It can be used to determine constitutional formulæ; for example, of the two diphenylhydrazines the symmetrical compound, $C_6H_5NH-NHC_6H_5$, gives two molecules of ethane, while the asymmetrical isomer, $(C_6H_5)_2N-NH_2$, gives only one.

Uranyl Sulphocyanide.—Paul Pascal.—Neutral uranysulphocyanide can be prepared by mixing two equimolecular solutions of uranyl sulphate and barium sulphocyanide. After filtration the red liquid is evaporated in a sulphuric vacuum. The residue is a dark red crystalline mass of formula $UO_2(CNS)_2 \cdot 8H_2O$. It is extraordinarily deliquescent, and readily dissolves in a trace of water. Its solutions possess all the properties of sulphocyanides and uranium salts. When enough pyridine is added to a solution of the sulphocyanide to cause the formation of a precipitate a crystalline basic sulphocyanide of formula $5UO_2(CNS)_2 + UO_3 + nH_2O$ is deposited. Double sulphocyanides can be formed by the addition of a metallic sulphocyanide to a solution of the uranyl salt. Such are $UO_2(CNS)_2 + 3NH_4CNS + 6H_2O$ and $UO_2(CNS)_2 + 5NH_4CNS + 2H_2O$. Only one series of salts is obtained with metals of the alkaline earths.

Action of Sodamide on 1,5-Diketones.—Edouard Bauer.—1,3-Dibenzoyl-2-phenyl propane when treated with sodamide is transformed into the disodium derivative, $C_6H_5-C(ONa)=CH-CH_2-CH=C(ONa)-C_6H_5$. This compound reacts with methyl iodide, and from the

product of the reaction the dimethyl derivative of dibenzoyl-propane can be isolated. Benzaldiacetophenone reacts similarly with sodamide, the final products of the reaction being ethylphenyl ketone and benzalpropionophenone.

Fixation of Sodium Methylene Compounds by Ethylenic Lactones.—Mihvoye Losanitch.—The unsaturated lactones can fix one molecule of sodium methylenic compounds, like substances possessing the group $-CO.CH=CH$. The author has studied this reaction in the case of Δ -angelic lactone, and has investigated the products formed. With sodium malonic ether 3-methylenedicarboxethyl-4-pentanolid is formed, and the corresponding compound with sodium cyanacetic ether. Sodium benzoylacetone simply causes the polymerisation of the lactone without entering directly into the reaction, while sodium alcoholate condenses the lactone according to the equation $2C_5H_6O_2 + H_2O = C_{10}H_{10}O_3$.

Hydroxylamine Derivatives of 1,4-Diketones and N-oxy-2,5-dimethylpyrrol.—E. E. Blaise.—The action of hydroxylamine upon diacetyl succinic ether is not similar to its action upon 1,4-diketones. In the former case N-oxyppyrrlic derivatives are obtained, while in the latter case only monoximes mixed with a small quantity of dioximes are formed. It seems logical to attribute this difference in behaviour to the presence in diacetylsuccinic ether of two carboxyls in the β -ketonic position.

Glycolate and Lactate of Uranyl and some Uranyl Salts of Polyacids of the Fatty Series.—G. Courtois.—The glycolate, lactate, oxalate, malonate, and succinate of uranyl can be obtained in the anhydrous state, and the three last possess hydrates of definite composition, those of the oxalate and malonate being trihydrates, while the succinate hydrates contain one and two molecules of water respectively. The tartrate forms two hydrates, one containing four and the other one molecule of water, while of the citrate three hydrates are known (hexa, di, and mono). Both tartrate and citrate firmly retain their last molecule of water, and cannot be dehydrated without undergoing decomposition.

Stereoisomeric Forms of Dibromide of Benzoyl-phenylacetylene.—Charles Dufraisse.—The author has isolated the two dibromides of benzoylphenylacetylene foretold by theory, and has found that the one which melts at 79° to 80° is pale yellow, while the other (m. p. 113° to 114°) is colourless. When treated with alcoholic potash they decompose into benzoic acid, hydrobromic acid, and bromphenylacetylene. When the isomer of melting-point 113° to 114° is treated with alcoholic potash an intermediate product is formed fusing at -11° to -10° , and rapidly isomerising under the influence of light. This substance is one of the two isomeric forms of the dibromide of phenyl acetylene.

β -Pentene and its Derivatives.—H. van Risseghem.—By dehydration in presence of paratoluene sulphonic acid the author has converted diethylcarbinol into β -pentene. The product has a constant melting-point and boiling-point, and hence only one of the stereoisomers foretold by theory is formed. This pentene is unaffected at ordinary temperatures by the action of ordinary isomerising agents, and hence forms a system in equilibrium. With bromine it yields a dibromopentane, which gives up hydrobromic acid in presence of alcoholic potash, giving a mixture of two position isomers of bromopentene. When this mixture is again treated with alcoholic potash β -pentene, already prepared by Favorsky, is obtained.

Ethylenic Isomerism of α -Bromopentenes.—G. Chavanne.—The author has prepared the two α -bromopentenes, and has determined their physical constants. He has observed that the molecular refractive power of the cis isomer is lower than that of the trans isomer. Neither form is stable at the ordinary temperature; each is spontaneously transformed into the other, and the stable state corresponds to a definite mixture of the two isomers.

THE CHEMICAL NEWS

VOL. CX., No. 2857.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

AUSTRALIA, 1914.

INAUGURAL ADDRESS OF THE PRESIDENT,
Prof. WILLIAM BATESON, M.A., F.R.S.

PART II.—SYDNEY.

AT Melbourne I spoke of the new knowledge of the properties of living things which Mendelian analysis has brought us. I indicated how these discoveries are affecting our outlook on that old problem of natural history, the origin and nature of Species, and the chief conclusion I drew was the negative one, that, though we must hold to our faith in the Evolution of Species, there is little evidence as to how it has come about, and no clear proof that the process is continuing in any considerable degree at the present time. The thought uppermost in our minds is that knowledge of the nature of life is altogether too slender to warrant speculation on these fundamental subjects. Did we presume to offer such speculations they would have no more value than those which alchemists might have made as to the nature of the elements. But though in regard to these theoretical aspects we must confess to such deep ignorance, enough has been learnt of the general course of heredity within a single species to justify many practical conclusions which cannot in the main be shaken. I propose now to develop some of these conclusions in regard to our own species, Man.

In my former Address I mentioned the condition of certain animals and plants which are what we call "polymorphic." Their populations consist of individuals of many types, though they breed freely together with perfect fertility. In cases of this kind which have been sufficiently investigated it has been found that these distinctions—sometimes very great and affecting most diverse features of organisation—are due to the presence or absence of elements, or factors as we call them, which are treated in heredity as separate entities. These factors and their combinations produce the characteristics which we perceive. No individual can acquire a particular characteristic unless the requisite factors entered into the composition of that individual at fertilisation, being received either from the father or from the mother or from both, and consequently no individual can pass on to his offspring positive characters which he does not himself possess. Rules of this kind have already been traced in operation in the human species; and though I admit that an assumption of some magnitude is involved when we extend the application of the same system to human characteristics in general, yet the assumption is one which I believe we are fully justified in making. With little hesitation we can now declare that the potentialities and aptitudes, physical as well as mental, sex, colours, powers of work or invention, liability to diseases, possible duration of life, and the other features by which the members of a mixed population differ from each other, are determined from the moment of fertilisation; and by all that we know of heredity in the forms of life with which we can experiment we are compelled to believe that these qualities are in the main distributed on a factorial system. By changes in the outward conditions of life the expression of some of these powers and features may be excited or restrained. For the development of some an external opportunity is needed, and if that be withheld the character is never seen, any more than if the

body be starved can the full height be attained; but such influences are superficial and do not alter the genetic constitution.

The factors which the individual receives from his parents and no others are those which he can transmit to his offspring; and if a factor was received from one parent only, not more than half the offspring, on an average, will inherit it. What is it that has so long prevented mankind from discovering such simple facts? Primarily the circumstance that as man must have *two* parents it is not possible quite easily to detect the contributions of each. The individual body is a *double* structure, whereas the germ-cells are *single*. Two germ cells unite to produce each individual body, and the ingredients they respectively contribute interact in ways that leave the ultimate product a medley in which it is difficult to identify the several ingredients. When, however, their effects are conspicuous the task is by no means impossible. In part also even physiologists have been blinded by the survival of ancient and obscurantist conceptions of the nature of man by which they were discouraged from the application of any rigorous analysis. Medical literature still abounds with traces of these archaisms, and, indeed, it is only quite recently that prominent horse-breeders have come to see that the dam matters as much as the sire. For them, though vast pecuniary considerations were involved, the old "homunculus" theory was good enough. We were amazed at the notions of genetic physiology which Prof. Baldwin Spencer encountered in his wonderful researches among the natives of Central Australia; but in truth, if we reflect that these problems have engaged the attention of civilised man for ages, the fact that he, with all his powers of recording and deduction, failed to discover any part of the Mendelian system is almost as amazing. The popular notion that any parents can have any kind of children within the racial limits is contrary to all experience, yet we have gravely entertained such ideas. As I have said elsewhere, the truth might have been found out at any period in the world's history if only pedigrees had been drawn the right way up. If, instead of exhibiting the successive pairs of progenitors who have contributed to the making of an ultimate individual, some one had had the idea of setting out the posterity of a single ancestor who possessed a marked feature such as the Hapsburg lip, and showing the transmission of this feature along some of the descending branches and the permanent loss of the feature in collaterals, the essential truth that heredity can be expressed in terms of presence and absence must have at once become apparent. For the descendant is not, as he appears in the conventional pedigree, a sort of pool into which each tributary ancestral stream has poured something, but rather a conglomerate of ingredient-characters taken from his progenitors in such a way that some ingredients are represented and others are omitted.

Let me not, however, give the impression that the unravelling of such descents is easy. Even with fairly full details, which in the case of man are very rarely to be had, many complications occur, often preventing us from obtaining more than a rough general indication of the system of descent. The nature of these complications we partly understand from our experience of animals and plants which are amenable to breeding under careful restrictions, and we know that they are mostly referable to various effects of interaction between factors by which the presence of some is masked.

Necessarily the clearest evidence of regularity in the inheritance of human characteristics has been obtained in regard to the descent of marked abnormalities of structure and congenital diseases. Of the descent of ordinary distinctions such as are met with in the normal healthy population we know little for certain. Hurst's evidence, that two parents both with light-coloured eyes—in the strict sense, meaning that no pigment is present on the front of the iris—do not have dark-eyed children, still stands almost alone in this respect. With regard to the inheritance of other colour-characteristics some advance

has been made, but everything points to the inference that the genetics of colour and many other features in man will prove exceptionally complex. There are, however, plenty of indications of system comparable with those which we trace in various animals and plants, and we are assured that to extend and clarify such evidence is only a matter of careful analysis. For the present, in asserting almost any general rules for human descent, we do right to make large reservations for possible exceptions. It is tantalising to have to wait, but of the ultimate result there can be no doubt.

I spoke of complications. Two of these are worth illustrating here, for probably both of them play a great part in human genetics. It was discovered by Nilsson-Ehle, in the course of experiments with certain wheats, that several factors having the same power may co-exist in the same individual. These cumulative factors do not necessarily produce a cumulative effect, for any one of them may suffice to give the full result. Just as the pure-bred tall pea with its two factors for tallness is no taller than the cross-bred with a single factor, so these wheats with three pairs of factors for red colour are no redder than the ordinary reds of the same family. Similar observations have been made by East and others. In some cases, as in the Primulas studied by Gregory, the effect is cumulative. These results have been used with plausibility by Davenport and the American workers to elucidate the curious case of the mulatto. If the descent of colour in the cross between the negro and the white man followed the simplest rule, the offspring of two first-cross mulattos would be, on an average, one black: two mulattos: one white, but this is notoriously not so. Evidence of some segregation is fairly clear, and the deficiency of real whites may perhaps be accounted for on the hypothesis of cumulative factors, though by the nature of the case strict proof is not to be had. But at present I own to a preference for regarding such examples as instances of imperfect segregation. The series of germ-cells produced by the cross bred consists of some with no black, some with full black, and others with intermediate quantities of black. No statistical tests of the condition of the gametes in such cases exist, and it is likely that by choosing suitable crosses all sorts of conditions may be found, ranging from the simplest case of total segregation, in which there are only two forms of gametes, up to those in which there are all intermediates in various proportions. This at least is what general experience of hybrid products lead me to anticipate. Segregation is somehow effected by the rhythms of cell-division, if such an expression may be permitted. In some cases the whole factor is so easily separated that it is swept out at once; in others it is so intermixed that gametes of all degrees of purity may result. That is admittedly a crude metaphor, but as yet we cannot substitute a better. Be all this as it may, there are many signs that in human heredity phenomena of this kind are common, whether they indicate a multiplicity of cumulative factors or imperfections in segregation. Such phenomena, however, in no way detract from the essential truths that segregation occurs, and that the organism cannot pass on a factor which it has not itself received.

In human heredity we have found some examples, and I believe that we shall find many more, in which the descent of factors is limited by sex. The classical instances are those of colour blindness and hæmophilia. Both these conditions occur with much greater frequency in males than in females. Of colour blindness at least we know that the sons of the colour blind man do not inherit it (unless the mother is a transmitter) and do not transmit it to their children of either sex. Some, probably all, of the daughters of the colour-blind father inherit the character, and though not themselves colour-blind, they transmit it to some (probably, on an average, half) of their offspring of both sexes. For since these normal-sighted women have only received the colour-blindness from one side of their parentage, only half their offspring, on an average, can inherit it. The sons who inherit the colour-blindness

will be colour-blind, and the inheriting daughters become themselves again transmitters. Males with normal colour-vision, whatever their own parentage, do not have colour-blind descendants, unless they marry transmitting women. There are points still doubtful in the interpretation, but the critical fact is clear, that the germ-cells of the colour-blind man are of two kinds:—(i.) Those which do not carry on the affection and are destined to take part in the formation of sons; and (ii.) those which do carry on the colour-blindness and are destined to form daughters. There is evidence that the ova also are similarly predestined to form one or other of the sexes, but to discuss the whole question of sex determination is beyond my present scope. The descent of these sex-limited affections nevertheless calls for mention here, because it is an admirable illustration of factorial predestination. It moreover exemplifies that *parental polarity* of the zygote to which I alluded in my first Address, a phenomenon which we suspect to be at the bottom of various anomalies of heredity, and suggests that there may be truth in the popular notion that in some respects sons resemble their mothers and daughters their fathers.

As to the descent of hereditary diseases and malformations, however, we have abundant data for deciding that many are transmitted as dominants and a few as recessives. The most remarkable collection of these data is to be found in family histories of diseases of the eye. Neurology and dermatology have also contributed many very instructive pedigrees. In great measure the ophthalmological material was collected by Edward Nettleship, for whose death we so lately grieved. After retiring from practice as an oculist he devoted several years to this most laborious task. He was not content with hearsay evidence, but travelled incessantly, personally examining all accessible members of the families concerned, working in such a way that his pedigrees are models of orderly observation and recording. His zeal stimulated many younger men to take part in the work, and it will now go on, with the result that the systems of descent of all the common hereditary diseases of the eye will soon be known with approximate accuracy.

Give a little imagination to considering the chief deduction from this work. Technical details apart, and granting that we cannot wholly interpret the numerical results, sometimes noticeably more and sometimes fewer descendants of these patients being affected than Mendelian formulæ would indicate, the expectation is that in the case of many diseases of the eye a large proportion of the children, grandchildren, and remoter descendants of the patients will be affected with the disease. Sometimes it is only defective sight that is transmitted; in other cases it is blindness, either from birth or coming on at some later age. The most striking example perhaps is that of a form of night-blindness still prevalent in a district near Montpellier, which has affected at least 130 persons, all descending from a single affected individual* who came into the country in the seventeenth century. The transmission is in every case through an affected parent, and no normal has been known to pass on the condition. Such an example well serves to illustrate the fixity of the rules of descent. Similar instances might be recited relating to a great variety of other conditions, some trivial, others grave.

At various times it has been declared that men are born equal, and that the inequality is brought about by unequal opportunities. Acquaintance with the pedigrees of disease soon shows the fatuity of such fancies. The same conclusion, we may be sure, would result from the true representation of the descent of any human faculty. Never since Galton's publications can the matter have been in any doubt. At the time he began to study family histories

* The first human descent proved to follow Mendelian rules was that of a serious malformation of the hand studied by Farabee in America. Drinkwater subsequently worked out pedigrees for the same malformation in England. After many attempts, he now tells me that he has succeeded in proving that the American family and one of his own had an abnormal ancestor in common, five generations ago.

even the broad significance of heredity was frequently denied, and resemblances to parents or ancestors were looked on as interesting curiosities. Inveighing against hereditary political institutions, Tom Paine remarks that the idea is as absurd as that of an "hereditary wise man," or an "hereditary mathematician," and to this day I suppose many people are not aware that he is saying anything more than commonly foolish. We, on the contrary, would feel it something of a puzzle if two parents, both mathematically gifted, had any children *not* mathematicians. Galton first demonstrated the overwhelming importance of these considerations, and had he not been misled, partly by the theory of pangenesis, but more by his mathematical instincts and training, which prompted him to apply statistical treatment rather than qualitative analysis, he might, not improbably, have discovered the essential of facts of Mendelism.

It happens rarely that science has anything to offer to the common stock of ideas at once so comprehensive and so simple that the courses of our thoughts are changed. Contributions to the material progress of mankind are comparatively frequent. They result at once in application. Transit is quickened, communication is made easier, the food supply is increased, and population multiplied. By direct application to the breeding of animals and plants such results must even flow from Mendel's work. But I imagine the greatest practical change likely to ensue from modern genetic discovery will be a quickening of interest in the true nature of man and in the biology of races. I have spoken cautiously as to the evidence for the operation of any simple Mendelian system in the descent of human faculty; yet the certainty that systems which differ from the simpler schemes only in degree of complexity are at work in the distribution of characters among the human population cannot fail to influence our conceptions of life and of ethics, leading perhaps ultimately to modification of social usage. That change cannot but be in the main one of simplification. The eighteenth century made great pretence of a return to nature, but it did not occur to those philosophers first to inquire what nature is; and perhaps not even the patristic writings contain fantasies much further from physiological truth than those which the rationalists of the "Encyclopædia" adopted as the basis of their social schemes. For men are so far from being born equal or similar that to the naturalist they stand as the very type of a polymorphic species. Even most of our local races consist of many distinct strains and individual types. From the population of any ordinary English town as many distinct human breeds could in a few generations be isolated as there are now breeds of dogs, and, indeed, such a population in its present state is much what the dogs of Europe would be in ten years' time but for the interference of the fanciers. Even as at present constituted, owing to the isolating effects of instinct, fashion, occupation, and social class, many incipient strains already exist.

In one respect civilised man differs from all other species of animal or plant in that, having prodigious and ever-increasing power over nature, he invokes these powers for the preservation and maintenance of many of the inferior and all the defective members of his species. The inferior freely multiply, and the defective, if their defects be not so grave as to lead to their detention in prisons or asylums, multiply also without restraint. Heredity being strict in its action, the consequences are in civilised countries much what they would be in the kennels of the dog-breeder who continued to preserve all his puppies, good and bad: the proportion of defectives increases. The increase is so considerable that outside every great city there is a smaller town inhabited by defectives and those who wait on them. Round London we have a ring of such towns with some 30,000 inhabitants, of whom about 28,000 are defective, largely, though of course by no means entirely, bred from previous generations of defectives. Now, it is not for us to consider practical measures. As men of science we observe natural events and deduce conclusions

from them. I may perhaps be allowed to say that the remedies proposed in America, in so far as they aim at the eugenic regulation of marriage on a comprehensive scale, strike me as devised without regard to the needs either of individuals or of a modern State. Undoubtedly, if they decide to breed their population of one uniform puritan grey, they can do it in a few generations; but I doubt if timid respectability will make a nation happy, and I am sure that qualities of a different sort are needed if it is to compete with more vigorous and more varied communities. Everyone must have a preliminary sympathy with the aims of eugenicists both abroad and at home. Their efforts at the least are doing something to discover and spread truth as to the physiological structure of society. The spirit of such organisations, however, almost of necessity suffers from a bias towards the accepted and the ordinary, and if they had power it would go hard with many ingredients of Society that could be ill-spared. I notice an ominous passage in which even Galton, the founder of eugenics, feeling perhaps some twinge of his Quaker ancestry, remarks that "as the Bohemianism in the nature of our race is destined to perish, the sooner it goes the happier for mankind." It is not the eugenicists who will give us what Plato has called divine releases from the common ways. If some fancier with the catholicity of Shakespeare would take us in hand, well and good; but I would not trust even Shakespeares meeting as a committee. Let us remember that Beethoven's father was an habitual drunkard, and that his mother died of consumption. From the genealogy of the patriarchs also we learn—what may very well be the truth—that the fathers of such as dwell in tents, and of all such as handle the harp or organ, and the instructor of every artificer in brass and iron—the founders, that is to say, of the arts and the sciences—came in direct descent from Cain, and not in the posterity of the irreproachable Seth, who is to us, as he probably was also in the narrow circle of his own contemporaries, what naturalists call a *nomen nudum*.

Genetic research will make it possible for a nation to elect by what sort of beings it will be represented not very many generations hence, much as a farmer can decide whether his byres shall be full of shorthorns or Herefords. It will be very surprising indeed if some nation does not make trial of this new power. They may make awful mistakes, but I think they will try.

Whether we like it or not, extraordinary and far-reaching changes in public opinion are coming to pass. Man is just beginning to know himself for what he is—a rather long-lived animal, with great powers of enjoyment if he does not deliberately forego them. Hitherto superstition and mythical ideas of sin have predominantly controlled these powers. Mysticism will not die out: for those strange fancies knowledge is no cure; but their forms may change, and mysticism as a force for the suppression of joy is happily losing its hold on the modern world. As in the decay of earlier religions Ushabti dolls were substituted for human victims, so telepathy, necromancy, and other harmless toys take the place of eschatology and the inculcation of a ferocious moral code. Among the civilised races of Europe we are witnessing an emancipation from traditional control in thought, in art, and in conduct which is likely to have prolonged and wonderful influences. Returning to freer or, if you will, simpler conceptions of life and death, the coming generations are determined to get more out of this world than their forefathers did. Is it then to be supposed that when science puts into their hand means for the alleviation of suffering immeasurable, and for making this world a happier place, that they will demur to using those powers? The intenser struggle between communities is only now beginning, and with the approaching exhaustion of that capital of energy stored in the earth before man began it must soon become still more fierce. In England some of our great-grandchildren will see the end of the easily accessible coal, and, failing some miraculous discovery of available energy, a wholesale reduction in population. There are races who have

shown themselves able at a word to throw off all tradition and take into their service every power that science has yet offered them. Can we expect that they, when they see how to rid themselves of the ever-increasing weight of a defective population, will hesitate? The time cannot be far distant when both individuals and communities will begin to think in terms of biological fact, and it behoves those who lead scientific thought carefully to consider whither action should lead. At present I ask you merely to observe the facts. The powers of science to preserve the defective are now enormous. Every year these powers increase. This course of action must reach a limit. To the deliberate intervention of civilisation for the preservation of inferior strains there must sooner or later come an end, and before long nations will realise the responsibility they have assumed in multiplying these "cankers of a calm world and a long peace."

The definitely feeble-minded we may with propriety restrain, as we are beginning to do even in England, and we may safely prevent unions in which both parties are defective, for the evidence shows that as a rule such marriages, though often prolific, commonly produce no normal children at all. The union of such social vermin we should no more permit than we would allow parasites to breed on our own bodies. Further than that in restraint of marriage we ought not to go, at least not yet. Something too may be done by a reform of medical ethics. Medical students are taught that it is their duty to prolong life at whatever cost in suffering. This may have been right when diagnosis was uncertain and interference usually of small effect; but deliberately to interfere now for the preservation of an infant so gravely diseased that it can never be happy or come to any good is very like wanton cruelty. In private few men defend such interference. Most who have seen these cases lingering on agree that the system is deplorable, but ask where can any line be drawn. The biologist would reply that in all ages such decisions have been made by civilised communities with fair success both in regard to crime and in the closely analogous case of lunacy. The real reason why these things are done is because the world collectively cherishes occult views of the nature of life, because the facts are realised by few, and because between the legal mind—to which society has become accustomed to defer—and the seeing eye, there is such physiological antithesis that hardly can they be combined in the same body. So soon as scientific knowledge becomes common property, views more reasonable and, I may add, more humane, are likely to prevail.

To all these great biological problems that modern society must sooner or later face there are many aspects besides the obvious ones. Infant mortality we are asked to lament without the slightest thought of what the world would be like if the majority of these infants were to survive. The decline in the birth-rate in countries already over-populated is often deplored, and we are told that a nation in which population is not rapidly increasing must be in a decline. The slightest acquaintance with biology, or even school-boy natural history, shows that this inference may be entirely wrong, and that before such a question can be decided in one way or the other, hosts of considerations must be taken into account. In normal stable conditions population is stationary. The laity never appreciates, what is so clear to a biologist, that the last century and a quarter, corresponding with the great rise in population, has been an altogether exceptional period. To our species this period has been what its early years in Australia were to the rabbit. The exploitation of energy-capital of the earth in coal, development of the new countries, and the consequent pouring of food into Europe, the application of antiseptics, these are the things that have enabled the human population to increase. I do not doubt that if population were more evenly spread over the earth it might increase very much more; but the essential fact is that under any stable conditions a limit must be reached. A pair of wrens will bring off a dozen young every year, but each year you will find the same number of pairs

in your garden. In England the limit beyond which under present conditions of distribution increase of population is a source of suffering rather than of happiness has been reached already. Younger communities living in territories largely vacant are very probably right in desiring and encouraging more population. Increase may, for some temporary reason, be essential to their prosperity. But those who live, as I do, among thousands of creatures in a state of semi-starvation will realise that too few is better than too many, and will acknowledge the wisdom of Ecclesiasticus who said "Desire not a multitude of unprofitable children."

But at least it is often urged that the decline in the birth-rate of the intelligent and successful sections of the population I am speaking of the older communities—is to be regretted. Even this cannot be granted without qualification. As the biologist knows, differentiation is indispensable to progress. If population were homogeneous civilisation would stop. In every army the officers must be comparatively few. Consequently, if the upper strata of the community produce more children than will recruit their numbers some must fall into the lower strata and increase the pressure there. Statisticians tell us that an average of four children under present conditions is sufficient to keep the number constant, and as the expectation of life is steadily improving we may perhaps contemplate some diminution of that number without alarm.

In the study of history biological treatment is only beginning to be applied. For us the causes of the success and failure of races are physiological events, and the progress of man has depended upon a chain of these events, like those which have resulted in the "improvement" of the domesticated animals and plants. It is obvious, for example, that had the cereals never been domesticated cities could scarcely have existed. But we may go further, and say that in temperate countries of the Old World (having neither rice nor maize) populations concentrated in large cities have been made possible by the appearance of a "thrashable" wheat. The ears of the wild wheats break easily to pieces, and the grain remains in the thick husk. Such wheat can be used for food, but not readily. Ages before written history began, in some unknown place, plants, or more likely a plant, of wheat lost the dominant factor to which this brittleness is due, and the recessive, thrashable wheat resulted. Some man noticed this wonderful novelty, and it has been disseminated over the earth. The original variation may well have occurred once only, in a single germ-cell.

So must it have been with man. Translated into terms of factors, how has that progress in control of nature which we call civilisation been achieved? By the sporadic appearance of variations, mostly, perhaps all, consisting in a loss of elements, which inhibit the free working of the mind. The members of civilised communities, when they think about such things at all, imagine the process a gradual one, and that they themselves are active agents in it. Few, however, contribute anything but their labour; and except in so far as they have freedom to adopt and imitate, their physiological composition is that of an earlier order of beings. Annul the work of a few hundreds—I might almost say scores—of men, and on what plane of civilisation should we be? We should not have advanced beyond the mediæval stage without printing, chemistry, steam, electricity, or surgery worthy the name. These things are the contributions of a few excessively rare minds. Galton reckoned those to whom the term "illustrious" might be applied as one in a million, but in that number he is, of course, reckoning men famous in ways which add nothing to universal progress. To improve by subordinate invention, to discover details missed, even to apply knowledge never before applied, all these things need genius in some degree, and are far beyond the powers of the average man of our race; but the true pioneer, the man whose penetration creates a new world, as did that of Newton and of Pasteur, is inconceivably

rare. But for a few thousands of such men, we should perhaps be in the Palaeolithic era, knowing neither metals, writing, arithmetic, weaving, nor pottery.

In the history of Art the same is true, but with this remarkable difference, that not only are gifts of artistic creation very rare, but even the faculty of artistic enjoyment, not to speak of higher powers of appreciation, is not attained without variation from the common type. I am speaking, of course, of the non-Semitic races of modern Europe, among whom the power whether of making or enjoying works of art is confined to an insignificant number of individuals. Appreciation can in some degree be simulated, but in our population there is no widespread physiological appetite for such things. When detached from the centres where they are made by others most of us pass our time in great contentment, making nothing that is beautiful, and quite unconscious of any deprivation. Musical taste is the most notable exception, for in certain races—for example, the Welsh and some of the Germans—it is almost universal. Otherwise artistic faculty is still sporadic in its occurrence. The case of music well illustrates the application of genetic analysis to human faculty. No one disputes that musical ability is congenital. In its fuller manifestation it demands sense of rhythm, ear, and special nervous and muscular powers. Each of these is separable and doubtless genetically distinct. Each is the consequence of a special departure from the common type. Teaching and external influences are powerless to evoke these faculties, though their development may be assisted. The only conceivable way in which the people of England, for example, could become a musical nation would be by the gradual rise in the proportional numbers of a musical strain or strains until the present type became so rare as to be negligible. It by no means follows that in any other respect the resulting population would be distinguishable from the present one. Difficulties of this kind beset the efforts of anthropologists to trace racial origins. It must continually be remembered that most characters are independently transmitted and capable of such recombination. In the light of Mendelian knowledge the discussion whether a race is pure or mixed loses almost all significance. A race is pure if it breeds pure and not otherwise. Historically we may know that a race like our own was, as a matter of fact, of mixed origin. But a character may have been introduced by a single individual, though subsequently it becomes common to the race. This is merely a variant on the familiar paradox that in the course of time if registration is accurate we shall all have the same surname. In the case of music, for instance, the gift, originally perhaps from a Welsh source, might permeate the nation, and the question would then arise whether the nation, so changed, was the English nation or not.

Such a problem is raised in a striking form by the population of modern Greece, and especially of Athens. The racial characteristics of the Athenian of the fifth century B.C. are vividly described by Galton in "Hereditary Genius." The fact that in that period a population, numbering many thousands, should have existed, capable of following the great plays at a first hearing, revelling in subtleties of speech, and thrilling with passionate delight in beautiful things, is physiologically a most singular phenomenon. On the basis of the number of illustrious men produced by that age Galton estimated the average intelligence as at least two of his degrees above our own, differing from us as much as we do from the negro. A few generations later the display was over. The origin of that constellation of human genius which then blazed out is as yet beyond all biological analysis, but I think we are not altogether without suspicion of the sequence of the biological events. If I visit a poultry-breeder who has a fine stock of thoroughbred game fowls breeding true, and ten years later—that is to say ten fowl-generations later—I go again and find scarcely a recognisable game-fowl on the place, I know exactly what has happened. One or two birds of some other or of no breed must have

strayed in and their progeny been left undestroyed. Now in Athens we have many indications that up to the beginning of the fifth century so long as the phratries and gentes were maintained in their integrity there was rather close endogamy, a condition giving the best chance of producing a homogeneous population. There was no lack of material from which intelligence and artistic power might be derived. Sporadically these qualities existed throughout the ancient Greek world from the dawn of history, and, for example, the vase-painters, the makers of the Tanagra figurines, and the gem-cutters were presumably pursuing family crafts, much as are the actor-families* of England or the professorial families of Germany at the present day. How the intellectual strains should have acquired predominance we cannot tell, but in an in-breeding community homogeneity at least is not surprising. At the end of the sixth century came the "reforms" of Cleisthenes (507 B.C.), which sanctioned foreign marriages and admitted to citizenship a number not only of resident aliens but also of manumitted slaves. As Aristotle says, Cleisthenes legislated with the deliberate purpose of breaking up the phratries and gentes, in order that the various sections of the population might be mixed up as much as possible, and the old tribal associations abolished. The "reform" was probably a recognition and extension of a process already begun; but is it too much to suppose that we have here the effective beginning of a series of genetic changes which in a few generations so greatly altered the character of the people? Under Pericles the old law was restored (451 B.C.), but losses in the great wars led to further laxity in practice, and though at the end of the fifth century the strict rule was re-enacted that a citizen must be of citizen-birth on both sides, the population by that time may well have become largely mongrelised.

Let me not be construed as arguing that mixture of races is an evil: far from it. A population like our own, indeed, owes much of its strength to the extreme diversity of its components, for they contribute a corresponding abundance of aptitudes. Everything turns on the nature of the ingredients brought in, and I am concerned solely with the observation that these genetic disturbances lead ultimately to great and usually unforeseen changes in the nature of the population.

Some experiments of this kind are going on at the present time, in the United States, for example, on a very large scale. Our grandchildren may live to see the characteristics of the American population entirely altered by the vast invasion of Italian and other South European elements. We may expect that the Eastern States, and especially New England, whose people still exhibit the fine Puritan qualities with their appropriate limitations, absorbing little of the alien elements, will before long be in feelings and aptitudes very notably differentiated from the rest. In Japan, also, with the abolition of the feudal system and the rise of commercialism, a change in population has begun which may be worthy of the attention of naturalists in that country. Till the revolution the Samurai almost always married within their own class, with the result, as I am informed, that the caste had fairly recognisable features. The changes of 1868 and the consequent impoverishment of the Samurai have brought about a beginning of disintegration which may not improbably have perceptible effects.

How many genetic vicissitudes has our own peerage undergone! Into the hard-fighting stock of mediæval and Plantagenet times have successively been crossed the cunning shrewdness of Tudor statesmen and courtiers, the numerous contributions of Charles II. and his concubines, reinforcing peculiar and persistent attributes which popular imagination especially regards as the characteristic of peers, ultimately the heroes of finance and industrialism. Definitely intellectual elements have been sporadically added, with rare exceptions, however, from the ranks of

* For tables of these families, see the supplement to *Who's Who in the Theatre*.

lawyers and politicians. To this aristocracy art, learning, and science have contributed sparse ingredients, but these mostly chosen for celibacy or childlessness. A remarkable body of men, nevertheless; with an average "horse-power," as Samuel Butler would have said, far exceeding that of any random sample of the middle-class. If only man could be reproduced by budding what a simplification it would be! In vegetative reproduction heredity is usually complete. The Washington plum can be divided to produce as many identical individuals as are required. If, say, Washington, the statesman, or preferably King Solomon, could similarly have been propagated, all the nations of the earth could have been supplied with ideal rulers.

Historians commonly ascribe such changes as occurred in Athens, and will almost certainly come to pass in the United States, to conditions of life and especially to political institutions. These agencies, however, do little unless they are such as to change the breed. External changes may indeed give an opportunity to special strains, which then acquire ascendancy. The industrial developments which began at the end of the eighteenth century, for instance, gave a chance to strains till then submerged, and their success involved the decay of most of the old aristocratic families. But the demagogue who would argue from the rise of the one and the fall of the other that the original relative positions were not justifiable altogether mistakes the facts.

Conditions give opportunities but cause no variations. For example, in Athens, to which I just referred, the universality of cultivated discernment could never have come to pass but for the institution of slavery which provided the opportunity, but slavery was in no sense a cause of that development, for many other populations have lived on slaves and remained altogether inconspicuous.

The long standing controversy as to the relative importance of nature and nurture, to use Galton's "convenient jingle of words," is drawing to an end, and of the overwhelmingly greater significance of nature there is no longer any possibility of doubt. It may be well briefly to recapitulate the arguments on which naturalists rely in coming to this decision both as regards races and individuals. First as regards human individuals, there is the common experience that children of the same parents reared under conditions sensibly identical may develop quite differently, exhibiting in character and aptitudes a segregation just as great as in their colours or hair-forms. Conversely all the more marked aptitudes have at various times appeared and not rarely reached perfection in circumstances the least favourable for their development. Next, appeal can be made to the universal experience of the breeder, whether of animals or plants, that strain is absolutely essential, that though bad conditions may easily enough spoil a good strain, yet that under the best conditions a bad strain will never give a fine result. It is faith, not evidence, which encourages educationists and economists to hope so greatly in the ameliorating effects of the conditions of life. Let us consider what they can do and what they cannot. By reference to some sentences in a charming though pathetic book, "What Is, and What Might Be," by Mr. Edmund Holmes, which will be well known in the Educational Section, I may make the point of view of us naturalists clear. I take Mr. Holmes's pronouncement partly because he is an enthusiastic believer in the efficacy of nurture as opposed to nature, and also because he illustrates his views by frequent appeals to biological analogies which help us to a common ground. Wheat badly cultivated will give a bad yield, though, as Mr. Holmes truly says, wheat of the same strain in similar soil well cultivated may give a good harvest. But, having witnessed the success of a great natural teacher in helping unpromising peasant children to develop their natural powers, he gives us another botanical parallel. Assuming that the wild bullace is the origin of domesticated plums, he tells us that by cultivation the bullace can no doubt be improved so far as to become a better bullace, but by no

means can the bullace be made to bear plums. All this is sound biology; but translating these facts into the human analogy, he declares that the work of the successful teacher shows that with man the facts are otherwise, and that the average rustic child, whose normal ideal is "bullacehood," can become the rare exception, developing to a stage corresponding with that of the plum. But the naturalist knows exactly where the parallel is at fault. For the wheat and the bullace are both breeding approximately true, whereas the human crop, like jute and various cottons, is in a state of polymorphic mixture. The population of many English villages may be compared with the crop which would result from sowing a bushel of kernels gathered mostly from the hedges, with an occasional few from an orchard. If anyone asks how it happens that there are any plum-kernels in the sample at all, he may find the answer perhaps in spontaneous variation, but more probably in the appearance of a long-hidden recessive. For the want of that genetic variation, consisting probably, as I have argued, in loss of inhibiting factors, by which the plum arose from the wild form, neither food, nor education, nor hygiene can in any way atone. Many wild plants are half-starved through competition, and transferred to garden soil they grow much bigger; so good conditions might certainly enable the bullace population to develop beyond the stunted physical and mental stature they commonly attain, but plums they can never be. Modern statesmanship aims rightly at helping those who have got down as wildlings to come into their proper class; but let not any one suppose such a policy democratic in its ultimate effects, for no course of action can be more effective in strengthening the upper classes whilst weakening the lower.

In all practical schemes for social reform the congerial diversity, the essential polymorphism of all civilised communities must be recognised as a fundamental fact, and reformers should rather direct their efforts to facilitating and rectifying class-distinctions than to any futile attempt to abolish them. The teaching of biology is perfectly clear. We are what we are by virtue of our differentiation. The value of civilisation has in all ages been doubted. Since, however, the first variations were not strangled in their birth, we are launched on that course of variability of which civilisation is the consequence. We cannot go back to homogeneity again, and differentiated we are likely to continue. For a period measures designed to create a spurious homogeneity may be applied. Such attempts will, I anticipate, be made when the present unstable social state reaches a climax of instability, which may not be long hence. Their effects can be but evanescent. The instability is due not to inequality, which is inherent and congenital, but rather to the fact that in periods of rapid change like the present, convection-currents are set up such that the elements of the strata get intermixed and the apparent stratification corresponds only roughly with the genetic. In a few generations under uniform conditions these elements settle in their true levels once more.

In such equilibrium is content most surely to be expected. To the naturalist the broad lines of solution of the problems of social discontent are evident. They lie neither in vain dreams of a mystical and disintegrating equality, nor in the promotion of that malignant individualism which in older civilisations has threatened mortification of the humbler organs, but rather in a physiological co-ordination of the constituent parts of the social organism. The rewards of commerce are grossly out of proportion to those attainable by intellect or industry. Even regarded as compensation for a dull life, they far exceed the value of the services rendered to the community. Such disparity is an incident of the abnormally rapid growth of population, and is quite indefensible as a permanent social condition. Nevertheless, capital, distinguished as a provision for offspring, is a eugenic institution, and unless human instinct undergoes some profound and improbable variation, abolition

of capital means the abolition of effort; but as in the body the power of independent growth of the parts is limited and subordinated to the whole, similarly in the community we may limit the powers of capital, preserving so much inequality of privilege as corresponds with physiological fact.

At every turn the student of political science is confronted with problems that demand biological knowledge for their solution. Most obviously is this true in regard to education, the criminal law, and all those numerous branches of policy and administration which are directly concerned with the physiological capacities of mankind. Assumptions as to what can be done and what cannot be done to modify individuals and races have continually to be made, and the basis of fact on which such decisions are founded can be drawn only from biological study.

A knowledge of the facts of nature is not yet deemed an essential part of the mental equipment of politicians; but as the priest, who began in other ages as medicine-man, has been obliged to abandon the medical parts of his practice, so will the future behold the schoolmaster, the magistrate, the lawyer, and ultimately the statesman, compelled to share with the naturalist those functions which are concerned with the physiology of race.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION. AUSTRALIA, 1914.

By Prof. WILLIAM J. POPE, M.A., LL.D., F.R.S.,
President of the Section.

THE British Association has been firmly established as one of the institutions of our Empire for more than half a century past. The powerful hold which it has acquired probably arises from the welcome which every worker in science extends to an occasional cessation of his ordinary routine—a respite during which the details of the specific inquiry in hand may be temporarily cast aside, and replaced by leisurely discussion with colleagues on the broader issues of scientific progress.

The investigator, continually occupied with his own problems and faced with an ever-increasing mass of technical literature, ordinarily finds little time for reflection upon the real meaning of his work; he secures, in general, far too few opportunities of considering in a philosophical sort of way the past, present, and future of his own particular branch of scientific activity. It is not difficult to form a fairly accurate survey of the position to which Chemistry had attained a generation ago, perhaps even a few years ago; probably no intellect at present existing could pronounce judgment upon the present position of our science in terms which would commend themselves to the historian of the twenty-first century. Doubtless even one equipped with a complete knowledge of all that has been achieved, standing on the very frontier of scientific advance and peering into the surrounding darkness, would be quite incompetent to make any adequate forecast of the conquests which will be made by chemical and physical science during the next fifty years. At the same time, chemical history tells us that progress is the result in large measure of imperfect attempts to appreciate the present and to forecast the future. I therefore propose to lay before you a sketch of the present position of certain branches of chemical knowledge and to discuss the directions in which progress is to be sought; none of us dare cherish the conviction that his views on such matters are correct, but everyone desirous of contributing towards the development of his science must attempt an appreciation of this kind. The importance to the worker and to the subject of free ventilation and discussion of the point of view taken by the individual can scarcely be over-estimated.

The two sciences of Chemistry and Physics were at one

time included as parts of the larger subject entitled Natural Philosophy, but in the early part of the nineteenth century they drew apart. Under the stimulus of Dalton's atomic theory, Chemistry developed into a study of the interior of the molecule, and, as a result of the complication of the observed phenomena, progressed from stage to stage as a closely reasoned mass of observed facts and logical conclusions. Physics, less entangled in its infancy with numbers of experimental data which apparently did not admit of quantitative correlation, was developed largely as a branch of applied mathematics; such achievements of the formal Physics of the last century as the mathematical theory of light and the kinetic theory of gases are monuments to the powers of the human intellect.

The path of Chemistry, as an application of pure logical argument to the interpretation of complex masses of observations, thus gradually diverged from that taken by Physics as the mathematical treatment of less involved experimental data, although both subjects derived their impetus to development from the speculations of genius.

It is interesting to note, however, that during recent years the two sciences, which were so sharply distinguished twenty years ago as to lead to mutual misunderstandings, are now converging. Many purely chemical questions have received such full quantitative study that the results are susceptible to attack by the methods of the mathematical physicist; on the other hand, the intense complication perceived during the fuller examination of many physical problems has led to their interpretation by the logical argument of the chemist, because the traditional mathematical mode of attack of the physicist has proved powerless to deal with the intricacies exhibited by the observed facts.

The progress of Chemistry during the last century has been mainly the result of the co-ordination of observed facts in accordance with a series of hypotheses each closely related in point of time to the one preceding it. The atomic theory, as it was enunciated by Dalton in 1803, was a great impetus to chemical investigation, but proved insufficient to embrace all the known facts; it was supplemented in 1813 by Avogadro's theorem—that equal volumes of gases contain the same numbers of molecules at the same temperature and pressure. These two important theoretical developments led to the association of a definite physical meaning with the idea of molecular composition, but ultimately proved insufficient for the interpretation of the ever-increasing mass of chemical knowledge collected under their stimulus. A further great impetus followed the introduction by Frankland and Kekulé, in 1852 onwards, of the idea of valency and the mode of building up constitutional formulæ; the conception of molecular constitution thus arose as a refinement on the Daltonian notion of molecular composition. In course of time the theoretical scheme once more proved insufficient to accommodate the accumulated facts, until, in 1874, van't Hoff and Le Bel demonstrated the all-important part which molecular configuration plays in the interpretation of certain classes of phenomena known to the organic Chemist.

During the early days of chemical science—those of Dalton's time and perhaps also those of Frankland and Kekulé—we can believe that chemical theory may have lacked the physical reality which it now seems to us to present; the attitude of our predecessors towards the theoretical interpretation of their observations was rather that described by Plato:—"As when men in a dark cavern judge of external objects by the shadows which they cast into the cavern." In the writings of the most clear-sighted of our forerunners we can detect an underlying suspicion of a possibility that, at some time or other, the theory by means of which chemical observations are held together may undergo an entire reconstruction; a very few years ago Ostwald made a determined attempt to treat our science without the aid of the molecular hypothesis, and, indeed, suggested the desirability of giving the Daltonian atomic theory decent burial.

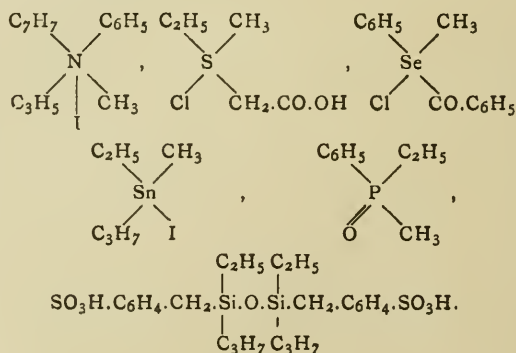
The last ten years or so has seen a change in this attitude. The development of Organic Chemistry has revealed so complete a correspondence between the indications of the conception of molecular constitution and configuration and the observed facts, and recent work on the existence of the molecule, largely in connection with colloids, with radio-activity, and with crystal structure, is so free from ambiguity, that persistence of doubt seems unreasonable. Probably most chemists are prepared to regard the present doctrine of chemical constitution and configuration as proven; although they may turn a dim vision towards the next great development, they have few misgivings as to the stability of the position which has already been attained.

Let us consider how far the study of Organic Chemistry has hitherto led us; we may pass over the gigantic achievements of those who in past generations determined constitution and performed syntheses, thus making the subject one of the most perfect examples of scientific classification which exist, and turn to the question of molecular configuration. In 1815 Biot observed that certain liquid organic substances deflect the plane of polarisation of a transmitted ray of light either to the right or to the left; half a century later Pasteur and Paternò pointed the obvious conclusion, namely, that the right- or left-handed deviation thus exerted must be due to a corresponding right- or left-handedness in the configuration of the chemical molecule. A scheme representing such right- or left-handedness, or enantiomorphism, was first enunciated by van't Hoff and Le Bel upon the basis of the previously established doctrine of chemical constitution; briefly stated, the idea suggested was that the methane molecule, CH_4 , was not to be regarded as extended in a plane in the manner represented by the Frankland-Kekulé constitutional formula, but as built up symmetrically in three-dimensional space. The carbon atom of the methane molecule thus occupies the centre of a regular tetrahedron, of which the apices are replaced by the four hydrogen atoms. A methane derivative, in which one carbon is separately attached to four different univalent atoms or radicles of the type CXYZW , should thus exist in two enantiomorphous configurations, one exhibiting right- and the other left-handedness. The inventors of this daringly mechanistic interpretation of the far less concrete constitutional formulæ were able to interpret immediately a large number of known facts, previously incomprehensible, by means of their extension of the Frankland-Kekulé view of constitution. They showed that every substance then known, which in the liquid state exhibited so-called optical activity, could be regarded as a derivative of methane in which the methane carbon atom was attached to four different univalent atoms or groups of atoms; a methane carbon atom so associated is termed an asymmetric carbon atom. It is of interest to note that the van't Hoff-Le Bel deduction resulted from the discussion of the behaviour of organic substances of some molecular complexity; the optically active substances then known were mostly the products of animal or vegetable life, and among them none occurs which contains less than three carbon atoms in the molecule. Lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, is practically the most simple optically active substance of natural occurrence; it contains twelve atoms in the molecule, and it has only recently been found possible to associate optical activity with a much more simply constituted substance, namely, chloriodomethanesulphonic acid, CHClSO_3H , the molecule of which contains less than 5 per cent of carbon and only nine atoms, four more than the minimum number, five, which theoretically can give rise to optical activity (Pope and Read, *Trans. Chem. Soc.*, 1914, cv., 811).

The working out of the practical consequences of the doctrine of the tetrahedral configuration of the methane carbon atom by von Baeyer, Emil Fischer, and Wislicenus is now a matter of history; the acquisition of masses of experimental data, broad in principle and minute in detail, placed the van't Hoff-Le Bel hypothesis beyond dispute.

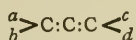
The rapid growth of Organic Chemistry as a classified subject contrasted strongly with that of Inorganic Chemistry, in which the collection of a great variety of detailed knowledge incapable of far-reaching logical correlation formed the most striking feature; in fact, the extension of the conclusion, proven in the case of carbon compounds, that the Frankland-Kekulé constitutional formulæ must be translated into terms of three-dimensional space, to compounds of elements other than carbon, did not immediately follow the application of the theory to this element. Twenty years ago, indeed, the idea prevailed that carbon compounds differed radically from those of other elements, and we were not prepared to transfer theoretical conclusions from the organic to the inorganic side of our subject. In 1891, however, Le Bel stated that he had found optical activity associated with asymmetry of a quinquivalent nitrogen atom; although the experimental work upon which this conclusion was founded is now known to be incorrect (*Trans. C. S.*, 1912, ci., 519), the conception thus put forward was important, as suggesting that the notion of space-configuration could not be restricted logically to methane derivatives. When it was proved in 1899 that benzylphenylallylmethylammonium iodide could exist in a right- and left-handed configuration, it became necessary to admit that the spacial arrangement of the parts of a chemical molecule, previously restricted to methane derivatives, must be extended to ammonium salts (Pope and Peachey, *Trans. Chem. Soc.*, 1899, lxxv., 1127).

The demonstration that optical activity, or enantiomorphism, of molecular configuration is associated not only with the presence of an asymmetric quadrivalent carbon atom, but also with that of a nitrogen atom attached to five different radicles, was the result of an improvement of technique in connection with the study of optical activity; previously the resolution into optically active components of a potentially optically active basic substance had been attempted with the aid of naturally occurring optically active weak acids of the general type of *d*-tartaric acid. The application of the strong *d*- and *l*-bromocamphorsulphonic acids and the *d*- and *l*-camphorsulphonic acids to such purposes rendered possible the isolation of the optically active substances containing no asymmetric atom other than one of quinquivalent nitrogen. The resolution of asymmetric quaternary ammonium salts of the kind indicated was rapidly followed by the preparation of optically active substances in which the enantiomorphism is associated with the presence of an asymmetric sulphur, selenium, tin, phosphorus, or silicon atom; compounds of the following constitutions were thus obtained in optically active modifications:—

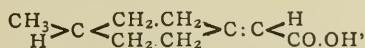


In all this work, and amongst all the varied classes of optically active compounds prepared, it was in every instance possible to indicate one particular quadrivalent or quinquivalent atom in the molecule which is separately attached to four or five different atoms or radicles; the enantiomorphism of molecular configuration may be

detected, in fact, by the observation that such an asymmetric atom is present. It must, however, be insisted that the observed optical activity is the result of the enantiomorphism of the molecular configuration; the asymmetry of a particular atom is not to be regarded as the cause of the optical activity but merely as a convenient geometrical sign of molecular enantiomorphism. In 1874 van't Hoff realised that molecular enantiomorphism and optical activity might conceivably exist without the presence of an asymmetric carbon atom, and suggested that compounds of the type—

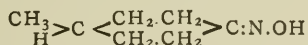


should be of this kind. Previously this particular case had escaped realisation experimentally, but an example fulfilling similar conditions was described in 1909; in this year the *d*- and *l*-isomerides of 1-methylcyclohexylidene-4-acetic acid—



were obtained (Perkin, Pope, and Wallach, *Trans. Chem. Soc.*, 1909, xcv., 1789; Perkin and Pope, *Trans. Chem. Soc.*, 1911, xcix., 1510). The consideration of the constitution of these substances shows no carbon atom which is attached to four different groups, but a study of the solid model representing the molecular configuration built up in accordance with the van't Hoff-Wislicenus conclusions reveals the enantiomorphism.

It is of some importance to note that the configurations assigned in such optically active substances as have been mentioned above, on the basis of the experimental evidence, are of as symmetrical a character as the conditions permit; the Kekulé formula for methane, CH_4 , in which all five atoms lie in the same plane, is not of so highly symmetrical a character as the van't Hoff-Le Bel configuration in which the four hydrogen atoms are situate at the apices of a regular tetrahedron described about the carbon atom as centre. Some influence seems to be operative which tends to distribute the component radicles in an unsymmetrical molecule in as symmetrical a manner as possible; recent work indicates, however, that this is not always true. During the past few years Mills and Bain (*Trans. Chem. Soc.*, 1910, xcvi., 1866) have shown that the synthetic substance of the constitution—



can be resolved into optically active modifications. The conclusion is thus forced upon us that the trivalent nitrogen atom in such compounds is not environed in the most symmetrical manner possible by the surrounding components of the molecule; the experimental verification which the conclusions of Hantzsch and Werner, concerning the isomerism of the oximes, thus derive, constitutes the first really direct evidence justifying their acceptance.

Quite recently, and by the application largely of the optically active powerful sulphonic acids derived from camphor, Werner has made another great advance in connection with the subject of optical activity. He has obtained a number of complex compounds of chromium, cobalt, iron, and rhodium in optically active modifications.

The foregoing brief statement probably suffices to indicate the progress which has been made during the last twenty years in demonstrating that the atoms or radicles associated in the chemical molecule do not lie in one plane but are disposed about certain constituent atoms in three-dimensional space; careful study of the present stage of progress shows that we must attribute to molecular configuration, as determined by modern chemical methods, a very real significance. It can no longer be supposed to possess the purely diagrammatic character which attached to the Frankland-Kekulé constitutional formulæ; it seems to be proved that the men who developed the doctrine of valency were not merely pursuing

an empirical mode of classification, capable of various modes of physical interpretation, but were devising the main scheme of a correct mechanical model of the chemical universe.

The development of a branch of science such as that now under discussion is, to a considerable extent, an artistic pursuit; it calls for the exercise of manipulative skill, of a knowledge of materials, and of originality of conception, which probably originate in intuition and empiricism, but must be applied with scientific acumen and logical judgment. For reasons of this kind many gaps occur in our present knowledge of the subject; although so many important conclusions find an unshakable foundation on facts relating to optical activity, we have as yet no clear idea as to why substances of enantiomorphous molecular configuration exhibit optical activity. Great masses of quantitative data referring to optical activity have been accumulated; something has been done towards their correlation by Armstrong, Frankland, Pickard, Lowry, and others, but we still await from the mathematical physicist a theory of optical activity comparable in quantitative completeness to the electro-magnetic theory of light. Until we get such a theory it seems unlikely that much further progress will be made in interpreting quantitative determinations of rotation constants.

That aspect of stereochemistry which has just been so briefly reviewed represents a situation which has been attained during the natural development of Organic Chemistry by methods which have now become traditional; progress has been made by the application of strictly logical methods of interpretation to masses of experimental data, and each new conclusion has been checked and verified by the accumulation of fresh contributions in the laboratory. The sureness of the methods adopted could not fail to lead to the intrusion of stereochemistry into adjacent fields of scientific activity; bio-chemistry, the study of the chemical processes occurring in living organisms, is already largely dominated by stereochemistry, and the certainty with which stereochemistry has inspired us as to the reality of the molecular constitution of matter is exerting a powerful influence in other branches of natural science. Quite possibly, however, the acquaintance which every chemist possesses of the great progress already made upon one particular set of lines is to some extent an obstacle to his appreciation of new directions in which further great stereochemical advances may be anticipated.

A little reflection will show that the study of the relation between the crystalline form and chemical constitution or configuration of substances in general may confidently be expected to lead to important extensions of our knowledge of the manner in which the atoms are arranged in molecular complexes. The earlier crystallographic work of the nineteenth century led to the conclusion that each substance affects some particular crystalline form, that the regular external crystalline shape is an expression of the internal structure of the crystal, and that a determination of the simpler properties—geometrical, optical, and the like—of a crystalline material constitutes a mode of completely characterising the substance. Later work during the last century demonstrated that the properties of crystalline substances are in entire harmony with a simple assumption as to the manner in which the units or particles of the material are arranged; the assumption is that the arrangement is a geometrically "homogeneous" one, namely, an arrangement in which similar units are uniformly repeated throughout the structure, corresponding points presenting everywhere a similar environment. The assumption of homogeneity of structure imposes a definite limitation upon the kinds of arrangement which are possible in crystals; it leads to the inquiry as to how many types of homogeneous arrangement of points in space are possible, and to the identification of these types with the known classes of crystal symmetry. The final conclusion has been attained that there are 230 geometrically homogeneous modes of distributing units, or points representing material particles, throughout space; these, the so-called

230 homogeneous "point-systems," fall into the thirty-two types of symmetry exhibited by crystalline solids. The solution of the purely geometrical problem here involved was commenced by Frankenheim in 1830, and finally completed by Barlow in 1894; it brings us face to face with the much larger stereochemical problem—that of determining what the units are which become homogeneously arranged in the crystal, why they become so arranged, and in what way a connection can be established between chemical constitution and crystal structure.

Since the conception of homogeneity of structure alone is clearly insufficient for the interpretation of the more advanced problem, some further assumption must be made as a foundation for any really comprehensive attempt to collate the quantities of isolated facts bearing upon the subject. Of the many assumptions which have been made in this connection only one, which may now be stated, has as yet proved fruitful in the sense that it serves to corre-

density of packing of the centres, the distance separating nearest centres is a maximum. Two homogeneous arrangements of points fulfil this condition, and these exhibit the symmetry of the cubic and the hexagonal crystalline systems.

Since the nature of the two arrangements of points is not easily realised by mere inspection, the systems must be presented in some alternative form for the purpose of more clearly demonstrating their properties; this is done conveniently by imagining each point in either arrangement to swell as a sphere until contact is made with the neighbouring points. The two arrangements then become those shown in Figs. 1 and 2, and are distinguished as the cubic and hexagonal closest-packed assemblages of equal spheres; they differ from all other homogeneous arrangements in presenting maximum closeness of packing of the component spheres. The equilibrium condition previously remarked—that, with a given density of distribution of

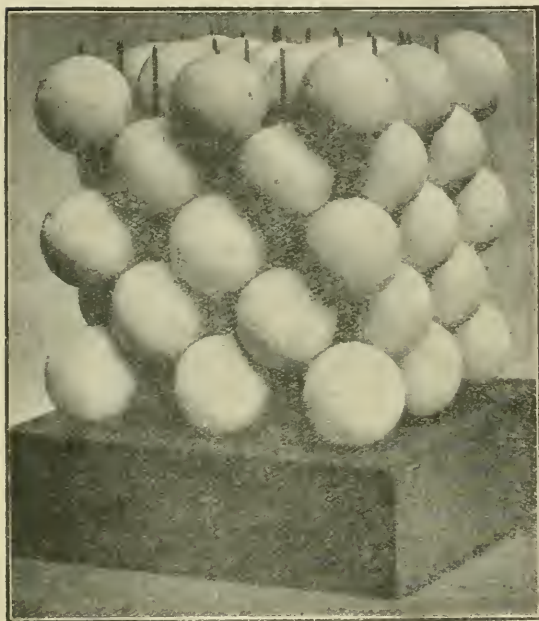


FIG. 1.

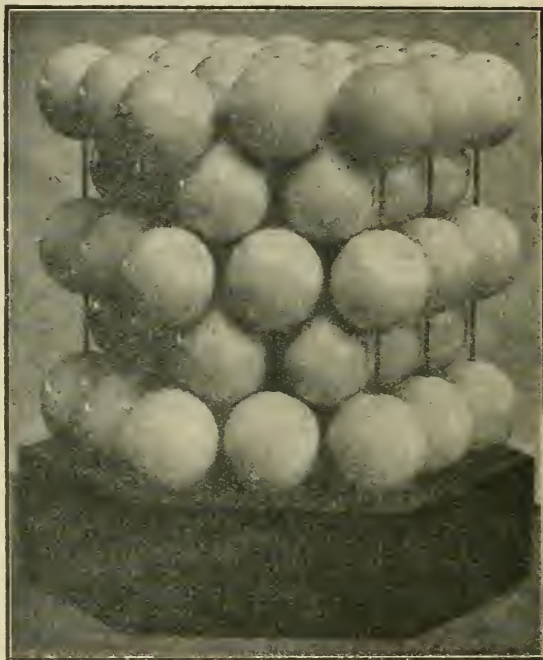


FIG. 2.

late large numbers of known experimental facts, and that it indicates the way to the discovery of fresh facts. The assumption is that each atom in a crystalline structure acts as a centre of operation of two opposing forces: (a) a repellent force, attributable to the kinetic energy of the atom, and (b) an attractive force, both forces, like gravity, being governed by some inverse distance law. Such an assumption forms an essential part of the classical work of Clerk Maxwell and van der Waals on the kinetic theory of gases and liquids. Its application to solid crystalline substances, where it must be applied in conjunction with the principle of structural homogeneity, was made by Barlow and myself in 1906.

The operation of the assumption just stated is readily visualised by considering the simplest possible case, that, namely, of a crystalline element, each molecule of which consists of but one atom and in which all the atoms are similar. Consideration of this kind of case shows that the set of identically similar centres of attracting and opposing forces will be in equilibrium when one particular simple condition is fulfilled; the condition is that, with a given

the force centres in space, the distance separating nearest is a maximum—is revealed in the assemblages of spheres as the condition that the spheres are arranged with the maximum closeness of packing.

A further step is yet necessary. Each point in the arrangements considered is regarded as the mean centre of an atom of the crystalline element, but the assumption originally made states nothing about the magnitude of the atom itself; it is therefore convenient to regard the whole of the available space as filled by the atoms, without interstices. This is conveniently done by imagining tangent planes drawn at each contact of sphere with sphere, so partitioning the available space into plane-sided polyhedra, each of which may be described as the domain of one component atom. The twelve-sided polyhedra thus derived from the cubic and the hexagonal assemblages represent the solid areas throughout which each atom exercises a predominant influence in establishing the equilibrium arrangement.

(To be continued).

THE GERMAN CHEMICAL TRADE.

THE Editor desires to call the attention of those readers who may be interested in, or concerned with, the manufacture of chemicals, to the opportunities which are now presented of engaging in the production of such materials, both inorganic and organic, but particularly the latter, as have hitherto been supplied from Germany and Austria.

The most important of these are medicinal drugs, aniline dyes, &c., and manufacturers who propose to extend their business in these or other directions will be furnished with authoritative information, particularly as regards Patent rights, the use of industrial alcohol, &c., on application (by letter) to Dr. J. C. CAIN, 24, Aylestone Avenue, Brondesbury Park, N.W.

CORRESPONDENCE.

NATIONAL RELIEF FUND.

To the Editor of the Chemical News.

SIR,—We regret to say that the Subscription Sub-Committee of the National Relief Fund has heard of a good many cases in which use has been made of its name, or of the names of those connected with it, with the object of securing support for appeals which are quite unauthorised.

We hope you will be so good as to permit the appearance of this letter, the object of which is to inform your readers that they may be assured that any extravagant or grotesque appeals emanate from persons who have neither the authorisation nor the support of this Committee.—We are, &c.,

C. ARTHUR PEARSON } Joint Secretaries,
HEDLEY F. LE BAS } Subscription Sub-Committee,
FREDERICK PONSONBY } National Relief Fund.

York House, St. James's Palace, S.W.,
August 24, 1914.

NOTICES OF BOOKS.

Die Radio-elemente und das Periodische System. ("The Radio-elements and the Periodic System"). By Dr. K. FAJANS. Berlin: Julius Springer. 1914.

THIS pamphlet contains a reprint of an article which appeared recently in *Die Naturwissenschaften*. The author has done much valuable and highly original work on the radio-elements, which he describes in detail, and he gives a very clear historical account of the work of other investigators. The article, while probably not containing very much that will be found new by those who have been following the subject carefully in periodical literature, gives an excellent general summary of researches on the radio-elements and their positions in the Periodic Table. The question of the atomic weight of ordinary lead and lead of radio-active origin, which has been attracting a good deal of attention lately, is discussed in an appendix.

Heat Balance for Albert Hiorth's Electrical Blast-furnace. Kristiania: Trykt i Eksprestrykkeriet. 1914.

THIS pamphlet contains detailed estimates of the cost of production of iron and steel by the use of Hiorth's new electrical blast-furnace. The costs are compared with those of various other methods and appear to be very fairly

computed, while no extravagant claims are made for the furnace. The calculations have been made both for the case in which the fuel is charged with the ore and limestone in the furnace itself, and also when it is previously used for the production of gas. The author believes that by electric smelting satisfactory final products can be made with inferior raw materials, and that there is a possibility of the development of a huge steel industry in countries which possess water power and cheap fuels and ore.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 24, June 15, 1914.

Syntheses by Means of Sodamide. Alkylcyclopentanones obtained by Hydrogenation of Unsaturated Derivatives either followed or not by Alkylation.—A. Haller and R. Cornubert.—Cyclopentanone cannot be directly alkylated; when treated with sodamide and an alcoholic iodide it condenses with itself and gives only insignificant quantities of α -alkylcyclopentanones. β -Methylcyclopentanone behaves similarly, except that the yields of α -derivatives are better. In order to get good yields it is necessary to start with a cyclopentanone already substituted once or twice in the α and α' -position, and then to let the alkyl iodide act on the sodium derivative. All the $\alpha\alpha'\alpha''$ -tetra-alkylpentanones when heated with sodamide in a benzene hydrocarbon give rise to amides of substituted fatty acids, which can be regarded as tetra or penta alkyl valerianic acids, according as the original substance used is cyclopentanone or β -methylcyclopentanone. The dibenzylidene derivatives of cyclopentanones as well as the allyl derivatives can be transformed into the corresponding saturated compounds by direct hydrogenation in presence of reduced nickel. With an active cyclopentanone the successive introduction of 1, 2, 3, and 4 alkyl radicles in the α - and α' -positions with regard to the CO group reduces the specific rotatory power of the new molecules even when these radicles are allyl groups.

Preparation of Hydrates of Manganese Sulphate.—R. de Forcrand.—By crystallisation from solutions at 0° the author has obtained the heptahydrate of manganese sulphate, but not the hexahydrate. The efflorescence of the powdered tetrahydrate in the cold *in vacuo* gives after two weeks a dihydrate, and after three weeks a monohydrate. After some weeks $\text{MnSO}_4 + 0.51\text{H}_2\text{O}$ can be obtained by heating to 75° . The dihydrate can be obtained by starting with a cold saturated solution of $\text{MnSO}_4 + 4\text{H}_2\text{O}$, and heating to 98° . Thus a light pink crystalline product is obtained. If the heating is continued products containing 1.75, 1.51, or even 1.28 H_2O are formed.

Derivatives of Cyclopentadiene and its Dimer.—O. Grignard and Ch. Courtot.—Cyclopentadiene readily gives a magnesium derivative which undergoes many reactions. Thus with iodine it gives $\text{C}_5\text{H}_5\text{I}$, or a polymer, and with bromine a tribrom derivative, $\text{C}_5\text{H}_5\text{Br}_3$, which is unstable and readily yields a dimer. By the action of cyanogen chloride and subsequent saponification dicyclopentadiene dicarboxylic acid is obtained. This acid can also be obtained by the direct action of dry carbon dioxide upon the magnesium compound.

Reduction by Hydrogen of Nickel and Copper Oxides in presence of a Dehydrating Agent.—E.

Berger.—The reduction of oxides of copper and nickel is very considerably accelerated when the water formed during the reaction is absorbed. In the case of nickel an intermediate compound, nickelous oxide, Ni_2O , is formed. The author is investigating the reduction in the same circumstances of other oxides, especially those of cobalt and iron.

Oxidation and Reduction of Copper. — Jacques Joannis.—Alteration of pressure appears to have no effect upon the oxidation of copper, but the oxide formed very considerably reduces the velocity of the reaction. In reduction also the pressure seems to have no influence, but in this case it is difficult to draw definite conclusions in consequence of the part played by the velocity of condensation of the water vapour.

Bromination of Benzene and its Homologues. Catalytic Action of Manganese. — L. Gay, F. Ducelliez, and A. Raynaud.—In presence of manganese bromine and benzene react with one another at 75° , and the metal is not attacked. It also acts as a catalyst at the ordinary temperature. Manganese acts as a catalyst in the bromination of the homologues of benzene, but in some experimental conditions its action is masked; the reaction which is first accelerated by the metal afterwards becomes slower. There is therefore no object in employing it.

Thujone and Thujamenthone. — Marcel Godchot.—In presence of nickel and hydrogen thujone is transformed at 175° to 180° into thujamenthone (1,2-dimethyl-3-isopropyl-5-one-cyclopentane). The trimethylenic nucleus which forms part of the thujonic molecule is unstable, and the cyclopentanic nucleus, which is remarkably stable, is formed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvii., No. 9, 1914.

Synthesis of Optically Active Halogen Hydrines. — Emil Aderhalden and Egon Eichwald.—The authors have endeavoured to prepare optically active triglycerides by first obtaining active halogen hydrines. They find that dibrom-propylamine can readily be prepared from allylamine and that by means of *d*-tartaric acid it is split into its components. With sodium nitrite optically active dibromhydrin is obtained. By the removal of one bromine atom from this optically active compound active *d*- and *l*-epibromhydrin are formed, and the authors hope that they will thus obtain a series of biologically important compounds.

MISCELLANEOUS.

British Association for the Advancement of Science (*Australian Meeting, 1914*).—The Papers brought before Sections A and B were as follows:—

SECTION A.—MATHEMATICS AND PHYSICS.

Melbourne.

Prof. F. T. TROUTON—Presidential Address—Absorption and Adsorption of Solutions.

Prof. C. G. ABBOT—Proofs of the Sun's Variability.

Prof. W. M. HICKS—On the Magnetron as a Scattering Agent for α - and β -Rays.

Discussion on the Present State of the Problems of Australian Longitudes, opened by P. BARACCHI (Government Astronomer of Victoria).

Joint Meeting with Section B on the Structure of Atoms and Molecules, opened by Sir E. RUTHERFORD.

Speakers:—Prof. H. E. ARMSTRONG, W. M. HICKS, ORME MASSON, W. J. POPE, and others.

Prof. E. GOLDSTEIN—On Salts coloured by Cathode Rays. Discussion on Antarctic Meteorology, opened by Dr. G. C. SIMPSON (Indian Meteorological Office).

Prof. T. R. LYLE—Demonstration of a Mechanical Analogue of Wireless Telegraphic Circuits.

Prof. T. R. LYLE—Demonstration of a Wave-tracer.

P. BARACCHI—The Federal Observatory at Mount Stromlo.

Report of Committee appointed to aid the work of establishing a Solar Observatory in Australia.

Report of Committee on Seismological Observations.

Sydney.

Sir E. RUTHERFORD—Origin and Nature of the γ -Rays from Radium.

Dr. F. W. DYSON—Distribution in Space of the Stars near the North Pole.

J. M. PETRIE and H. G. CHAPMAN—Action of the Juice of *Euphorbia peplus* on a Photographic Plate.

Prof. O. W. VONWILLER—Photo-electric Effect in Selenium.

H. MOSELEY—High-frequency Spectra.

Prof. W. G. DUFFIELD—The Pressure upon the Poles of a Carbon Arc.

Joint Discussion with Section G on Wireless Telegraphy, opened by Sir O. J. LODGE.

Prof. J. A. POLLOCK—Some Measurements of the Wavelength in Air of Electrical Vibrations Associated with a Thin Straight Terminated Rod.

Prof. W. H. H. HUDSON—The Evolute of the Limaçon.

Prof. H. H. TURNER—Discontinuities in Meteorological Phenomena.

Prof. A. S. EDDINGTON—The Oblate Shape of the Stellar System.

Reports of Committees.

Brisbane.

Address to the Sub-section of Cosmical Physics by Prof. E. W. BROWN on the Motion of the Moon.

SECTION B.—CHEMISTRY.

Melbourne.

Prof. W. J. POPE—Presidential Address and Demonstration. Joint Meeting with Section A on the Structure of Atoms and Molecules (see above).

Prof. O. MASSON—A Device for the Representation of the Natural Classification of the Elements.

F. H. CAMPBELL—New Method for the Determination of Vapour Pressures and an Examination of a Source of Error in certain Dynamical Methods.

E. J. HARTUNG—New Method for Determining the Specific Heat of Liquids.

V. G. ANDERSON—Influence of Weather Conditions upon the Amounts of Nitrogen Acids in the Rainfall near Melbourne.

Sydney.

Joint Discussion with Section M on Metabolism.

Ninth International Congress of Applied Chemistry.

—The Executive Committee has issued a preliminary announcement of the meetings next year. The Congress is to be held at St. Petersburg from August 8–14, 1915, under the presidency of Professor P. J. Walden. The official languages are Russian, French, English, German, and Italian, and applications for membership are to be made not later than April 14 to the Treasurer of the Ninth International Congress of Applied Chemistry, 8, Winter Palace Place, St. Petersburg.

Beetroot Culture. — The fortnightly journal *La Betterave* is a useful review dealing with agricultural industries, and especially with those connected with beetroot culture. In the issues of May 24 and June 7 there are articles on the pests by which the beetroot is attacked and the best means to combat them, and tables are given showing the areas in European countries under beet in 1914, compared with those of the preceding year. France show a slight decrease in this respect, while in most other countries, especially Germany and Russia, there are large increases.

THE CHEMICAL NEWS

Vol. CX., No. 2858.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

AUSTRALIA, 1914.

By Prof. WILLIAM J. POPE, M.A., LL.D., F.R.S.,
President of the Section.

(Concluded from p. 106).

THE two assemblages can now be described in a quantitative manner by stating the symmetry and also the relative dimensions of each. The cubic assemblage exhibits symmetry identical with that of the cube or the regular octahedron, a symmetry characteristic of so-called holohedral cubic crystals; the relative dimensions in different directions are defined by the symmetry. The assemblage can, in fact, be referred to three axes parallel to the edges of a cube, and as these directions are obviously similar in a cube, their ratios are of the form, $a : b : c = 1 : 1 : 1$. This expression indicates that if the assemblage, supposed indefinitely extended through space, is moved by a unit distance in either of the three rectangular directions a , b , and c , the effect as examined from any point, is as if the assemblage had not been moved at all.

The symmetry of the hexagonal assemblage is identical with that of a hexagonal prism or of a double hexagonal pyramid, and is that characteristic of the so-called holohedral, hexagonal, crystalline system; the relative dimensions are no longer defined entirely by the symmetry, and are conveniently stated as the ratio of the diameter, a , of the prism or pyramid, to the height, c , of the pyramid. The ratio, $a : c$, for the assemblage of spheres under discussion can be calculated; it assumes two forms, corresponding to two modes of selecting alternative principal diameters of the prism as unit. The alternative ratios are: $a : c = 1 : 1.6330$ or $a : c = 1 : 1.4142$.

This somewhat lengthy theoretical discussion has now reached a stage at which it can be applied to the observed facts; the accompanying table (Table I.) states the mode in which crystalline substances of different degrees of molecular complexity distribute themselves amongst the various crystal systems. Of the elements which have been crystallographically examined, 50 per cent are cubic, whilst a further 35 per cent are hexagonal; and consideration of the data for these latter shows that they exhibit approximately the axial ratios characteristic of the hexagonal closest-packed assemblage; thus magnesium shows $a : c = 1 : 1.6242$, and arsenic the ratio $a : c = 1 : 1.4025$.

TABLE I.

System.	Per cent.	Inorganic substances, the number of atoms in the molecule of which is respectively :					Organic substances.
		Elements.					
		2.	3.	4.	5.	More than 5.	
Cubic	50	68.5	42	5	12	5.8	2.5
Hexagonal	35	19.5	11	35	38	14.6	4.0
Tetragonal	5	4.5	19	5	6	7	5.0
Orthorhombic ..	5	3.0	23.5	50	36	27.3	34.0
Monosymmetric ..	5	4.5	3	5	6	37.3	47.5
Anorthic	0	0	1.5	0	2	8	7.0
Number of cases examined for each vertical column .	140	67	63	20	50	673	585

Whilst the crystal structure of some 85 per cent of the crystalline elements seems to be in general agreement

with the simple assumption of equilibrium which has been made, the divergence presented by about 15 per cent of the elements still awaits explanation. The previous discussion applies to the theoretically simple case of a monoatomic element; many of the elements are, however, certainly polyatomic. Imagine, therefore, that in the crystal structure, agreeing with the cubic or hexagonal arrangement just described, the similar atoms are grouped to form complex molecules, each containing two or more atoms; the geometrical effect of this grouping, if any, should be, first, to degrade the symmetry of the structure, and, secondly, to slightly alter its relative dimensions. It would therefore be expected that if the elements which are neither cubic nor hexagonal owe their departure from those systems to molecular aggregation, the crystal dimensions should approximate closely to those of the two ideal assemblages; this is, indeed, found to be the case. Monosymmetric sulphur, for instance, exhibits the axial ratios $a : b : c = 0.9958 : 1.00988$, $\beta = 95.46'$; the relative dimensions in the three directions, a , b , and c , are almost the same as in the cubic system, and the angle between the directions a and c is $95.46'$, instead of 90° . This substance has nearly the dimensions of a cubic crystal, and is obviously "pseudo-cubic"; the same is true of all other elements which depart from true cubic or hexagonal symmetry.

The crystalline forms presented by the elements are consequently in accordance with the assumption that the crystal structures are equilibrium arrangements of the component atoms of the two kinds described. It is also indicated that aggregation of the atoms to form molecular complexes is responsible for the departure from simple cubic or hexagonal symmetry; in this connection it is interesting to note that the strongly coloured elements depart most widely from these two systems. Thus, the colourless modifications of carbon and phosphorus are cubic, whilst the black graphite is monosymmetric and the red phosphorus is orthorhombic in crystal form; this is in accordance with the general view that colour is the result of some particular kind of molecular aggregation.

Although so much general correspondence of a quantitative character is to be observed between the observed facts and the anticipations developed from the equilibrium assumption, it has become evident during the last year or two that the conception formed as to the nature of the equilibrium which determines the arrangement of the atoms in a crystalline element is of too simple a character. In 1912 Laue showed that on passing a narrow pencil of X-rays through a crystal plate the emergent rays were capable of forming a regular geometrical pattern of spots upon a photographic plate placed to receive the emergent beam; the pattern of spots thus produced was in agreement with the symmetry of the direction in the crystal plate in which the beam was passed. This discovery was developed and very considerably extended by Bragg, who was able to show that an X-ray beam undergoes reflection at the surface of a crystal plate. The interpretation of the novel results indicates that the homogeneous crystal structure acts upon the X-ray beam much as a solid diffraction grating might be expected to do, and that each deflected transmitted ray is a reflection from one set of parallel planes of atoms in the crystal.

The experimental and theoretical study of the X-ray effects has been prosecuted with brilliant success by W. H. and W. L. Bragg, the result being that a method is now available which makes it possible to determine with very great probability the actual arrangement of the constituent atoms in crystal structure. Sufficient time has not yet elapsed for the thorough exploitation of this new and fruitful field of research, but many data are available already for comparison with the conclusions drawn from the consideration of the equilibria possible in crystal structures; it is found that the two methods do not at once lead to identical conclusions. Thus, in accordance with the first method, the structure of the diamond would be indicated as some slight modification of the cubic

closest-packed assemblage of equal spheres, the modification consisting in the main of a grouping of sets of atoms which leads to the partial cubic symmetry which the diamond apparently exhibits; one particular mode of grouping which leads to the required result consists in supposing the carbon atoms formed into sets of four, tetrahedrally arranged, two oppositely orientated sets of such tetrahedral groups being distinguished. If each of these tetrahedral groups be replaced by a single point situated at the group-centre, the structure which the Bragg experiments indicate for the diamond is obtained.

The simple geometrical relationship which thus exists between the two suggested structures for diamond raises a suspicion that the particular form in which the assumption of equilibrium is stated requires qualification: that possibly the domain of the carbon atom when packed with others, as in the diamond, does not become converted into a rhombic dodecahedron, but into a polyhedron roughly tetrahedral in shape.

Leaving this particular point for the moment and turning again to Table I., it is seen that the binary compounds, like the elements, also tend to crystallise in the cubic or hexagonal systems; the axial ratios of the hexagonal binary compounds approximate very closely to the value, $a:c = 1:1.6330$, calculated for the closest-packed hexagonal assemblage of equal spheres. The values of c/a for all the known cases are: —BeO—1.6365, ZnO—1.6077, ZnS—1.6350, CdS—1.6218, and AgI—1.6392.

Assemblages representing the crystal structures of the cubic and hexagonal binary compounds may be derived from the two closest-packed assemblages of similar spheres already described, by homogeneously replacing one-half of the spheres by different ones of the same size. The degrees of symmetry presented by these arrangements are not so high as those of the unsubstituted assemblages; this is in accordance with the fact that the crystals themselves have not the full symmetry of the holohedral cubic or hexagonal system. Thus, on warming a hexagonal crystal of silver iodide, one end of the principal axis c becomes positively, and the other negatively, electrified. The axis c is thus a polar axis, having different properties at its two ends; this axis will be found to be polar in the model. Again, when hexagonal silver iodide is heated to 145° , it changes its crystalline form and becomes cubic; this so-called polymorphous change can be imitated in the hexagonal model by slightly shifting each pair of layers of spheres in the assemblage.

A very close agreement thus exists between the properties of the assemblages deduced and the observed properties of those binary compounds which crystallise in the cubic or hexagonal systems. The remaining 12 per cent or so are not, in general, pseudo-cubic or pseudo-hexagonal, and it is noteworthy that they comprise those binary compounds in which the two component elements have not the same lowest valency; amongst them are the substances of the compositions, PbO, FeAs, HgO, AsS, and CuO.

On comparing the structures of the binary crystalline compounds indicated by the foregoing method of consideration with those deduced by the Braggs, discrepancies are again obvious; again, however, the former assemblage is converted into the latter by replacing groups of spheres by their group-centres. The relation thus rendered apparent is once more a suggestion that the type of equilibrium conditions originally assumed is too simple. It will be seen, however, that the Bragg results furnish a proof of one part of the assumption made concerning equilibrium, namely, that each component atom operates separately; the discussion of the properties of crystals on the assumption that the crystal structure may be regarded as built up of similar mass-points, due to the mathematical physicists of the last century, therefore requires to be reopened. Thus, the Bragg structure of rock-salt is represented by dividing space into equal cubes by three sets of parallel planes, and replacing the cube corners encountered along the directions of the cube edges by chlorine and sodium

atoms alternately; each chlorine atom then has six sodium atoms as its nearest and equally distant neighbours. With which of the latter the one chlorine atom is associated to form a molecule of sodium chloride is not apparent from the nature of the crystal structure.

Time need not be now occupied with the further discussion of the crystalline structure of simple substances; until the discovery of the X-ray effects thus briefly described, no direct method of determining those structures was available, and, in view of the paucity of the experimental data, only the possibilities of arrangement could be considered in the light of the Barlow-Pope mode of treatment. It will, however, be useful to review some of the results which accrue from this latter method of regarding the problem of crystal structure in general.

Taking the general standpoint, which is also in accordance with the Bragg results, that each component atom of a crystalline structure has a separate spacial existence, and premising that the atomic domains are close-packed in the assemblage in accordance with some particular type of equilibrium law, it becomes obvious that crystalline structure presents a volume problem. The law arrived at after a careful investigation of the subject—the so-called law of valency volumes—states that in a crystalline structure, the component atoms occupy domains approximately proportional in volume to the numbers representing the fundamental valencies of the elements concerned; the student of the subject of molecular volumes will hardly accept this conclusion without convincing evidence of its correctness—it indicates, for instance, that in crystalline potassium sulphate, if the atomic volume of potassium is taken as unity, those of sulphur and oxygen each have the value two. Many different lines of crystallographic argument converge, however, to this law, and if the latter is in the end found to be incorrect, it at least represents something fundamental which still awaits enunciation in a more generally acceptable form. A few illustrative instances may be quoted.

If valency be a volume property, the relation should be revealed in the compositions of chemical substances, especially those of composite character. The sum of the valencies in potassium sulphate, K_2SO_4 , is 12, and in ammonium sulphate, $(NH_4)_2SO_4$, 24, just twice the number; the two substances are so closely related that they crystallise together to form "solid solutions" (isomorphous mixtures). Similarly, in the alums, such as $K_2SO_4 + Al_2(SO_4)_3 + 24H_2O$, the valencies are $12 + 36 + 96$; the sum of the valencies of the water present, 96, is just twice that, 48, of those exhibited by the metallic sulphates. Similar curious numerical relationships occur in each of the well-defined series of double salts.

Again, if the valency volume law hold for two substances of different crystalline form, such as orthorhombic rubidium nitrate, $RbNO_3$, and rhombohedral sodium nitrate, $NaNO_3$, the metal, the nitrogen, and the oxygen in each compound should have the respective atomic volumes 1, 3, and 2. As the substances differ in density the absolute values of the atomic volumes of nitrogen and oxygen will differ in the two substances as examined at the same temperature; the ratios of the atomic volumes in either compound should, however, be as stated. Considering this conclusion in conjunction with the fact that these crystalline compounds represent symmetrically constructed assemblages, it would seem that the relative dimensions of the one crystal structure should be traceable in those of the other. Orthorhombic rubidium nitrate exhibits the axial ratios, $a:b:c = 1.7336:1:0.7106$, three rectangular co-ordinates, a , b , and c , being used as the directions of reference; rhombohedral sodium nitrate exhibits $a:c = 1:0.8276$, the co-ordinates being three axes, a , making angles of 120° in one plane, and a fourth axis c , perpendicular to a . On converting the axial system of sodium nitrate into a simple set of rectangular axes similar to those used for rubidium nitrate, the value, $a:c = 1:0.8276$, becomes $a:b:c = 1.7320:1:0.7151$.

These values approximate very closely to those obtained

TABLE II.

	W.	$a : b : c$	x	y	z
$C_{10}H_{14}O_3$	60	1'0011 : 1 : 1'7270	3'2654	3'2618	5'6331
$C_{10}H_{16}O_4, \frac{1}{2}(CH_3)_2CO$	74	1'2386 : 1 : 1'7172	4'0435	3'2646	5'6060

TABLE III.

Minerals.	W.	Axial ratios.	Equivalent parameters.			z/W .
		$a : b : c$	x	y	z	
Chondrodite	34	1'08630 : 1 : 3'14472	2'3367	2'1510	6'7644	0'19895
Humite	48	1'08021 : 1 : 4'40334	2'3343	2'1610	9'5155	0'19824
Clinohumite	62	1'08028 : 1 : 5'65833	2'3384	2'1646	12'2491	0'19756
Prolectite—observed	20	1'0803 : 1 : 1'8862	2'3130	2'1414	4'0385	0'19977
Prolectite—calculated	20	1'0818 : 1 : 1'8618	2'3365	2'1589	4'0211	0'19968
Forsterite—observed	14	0'9296 : 1 : 1'1714	2'3426	2'1778	2'7442	0'19601
Forsterite—calculated	14	0'9240 : 1 : 1'1741	2'3365	2'1589	2'7433	0'19585

by direct measurement of the orthorhombic rubidium salt. It seems difficult to avoid the conclusion that the two dissimilar crystalline structures are built up by the arrangement of layers or blocks of the same relative dimensions in two different ways, the molecule of sodium nitrate, $NaNO_3$, possessing practically the same relative dimensions as that of rubidium nitrate, $RbNO_3$; this, of course, is in discord with the classic conception of atomic volume, but agrees entirely with the valency volume law.

Another remarkable body of evidence is found in the interpretation of many morphotropic relationships between organic and inorganic substances which have been long recognised but have hitherto eluded interpretation. The description of one or two cases will make the bearing of the law of valency volumes clear in this connection.

d-Camphoric anhydride, $C_{10}H_{14}O_3$, and *d* camphoric acid crystallised with acetone, $C_{10}H_{16}O_4, \frac{1}{2}(CH_3)_2CO$, both crystallise in the orthorhombic system, and exhibit the axial ratios stated in Table II.

The ratio c/b is approximately the same in the two cases, and general similarity exists between the two crystalline substances. It will be observed that the values of a/b are very nearly in the ratio of the sums of the valencies, W , making up the two molecular complexes, namely, $60 : 74 = 100 : 123$. This and similar cases may be more conveniently discussed with the aid of the so-called equivalence parameters; these are the edge lengths, x, y , and z , of a parallelepipedon of which the volume is W , the sum of the valencies in the molecule, and of which the linear and angular dimensions express the crystallographic axial ratios. Thus, for orthorhombic substance, $xyz = W$, and $x : y : z = a : b : c$; the equivalence parameters of the two substances under discussion are given in the table, and it will be seen that whilst y and z are almost identical for the two, the x values differ considerably. This correspondence indicates clearly that in passing from camphoric anhydride to the acetone compound of the acid the mass added to the molecular complex, $H_2O + \frac{1}{2}(CH_3)_2CO$, occupies a volume proportional to the number of valency units which it contributes to the structure.

A very remarkable relation has been long recognised between the crystalline forms of the three minerals chondrodite, $Mg_3(SiO_4)_2, 2Mg(F,OH)$, humite, $Mg_5(SiO_4)_3, 2Mg(F,OH)$, and clinohumite, $Mg_7(SiO_4)_4, 2Mg(F,OH)$; the crystalline forms are referable to three rectangular directions, a, b , and c , and the ratio $a : b$ is practically the same for all three minerals. The relationship is at once elucidated by the law of valency volumes in a simple manner. In the molecules of the three substances the sums of the valencies of the constituent atoms are respectively 34, 48, and 62; it follows from the law that these numbers are proportional to the relative volumes of the several molecules. The ratios, $a : b : c$, being known, the dimensions can be calculated of solid rectangular blocks having these volumes, and having edge lengths proportional to the axial ratios, $a : b : c$. The equivalence parameters, x, y , and z , thus calculated are given in

Table III.; the first observation of importance to be made is that equivalence parameters, x and y , remain practically constant throughout the series of three minerals.

It will be seen that chondrodite and humite, and humite and clinohumite, differ in molecular composition by the quantity, $Mg_2(SiO_4)$; they form a series in which the increment of composition is $Mg_2(SiO_4)$. Subtracting this increment from the composition of chondrodite, the residue, $Mg_2(SiO_4), 2Mg(F,OH)$, is left. This is the composition of the mineral prolectite, and the increment, $Mg_2(SiO_4)$, is the composition of the mineral forsterite.

If the law of valency volumes be correct the equivalence parameters of forsterite should be the x and y of the first three minerals, and a value z which is the difference between the z values of chondrodite and humite, or of humite and clinohumite; further, prolectite should have x and y values identical with those of the other four minerals, and a z value which is the difference of the z values of chondrodite and forsterite. It is thus possible to calculate the equivalence parameters of forsterite and prolectite without using data determined on these two minerals, and to compare the values so obtained with those calculated from the observed axial ratios of forsterite and prolectite. All the values referred to are given in Table III., and it will be obvious that the agreement between the calculated and the observed equivalence parameters is very close; as this agreement could not occur without the operation of the law of valency volumes, which was deduced from entirely different data, strong confirmation of the accuracy of the law is provided.

The several illustrations of the operation of the law of valency volumes have been quoted in detail for the purpose of showing how difficult it is to avoid the conclusion that this deduction represents some physical reality. It may be traced in connection with quantitative data of other kinds; during the last few years it has been very successfully applied by Le Bas to the interpretation of the molecular volumes of liquid substances.

From what has been already said it will be seen that the great problem as to the relation between crystal structure and chemical constitution, of which the solution seems imminent, is a stereochemical one; assemblages must be built up in accordance with the principle of homogeneity and in some form of close-packing, in which each component atom of a chemical molecule is represented as the sole occupant of some specific solid area. The properties of these assemblages must also be in agreement with the crystallographic measurements and the X-ray photographs yielded by the substances represented.

A brief indication may be given of what has been already effected in this connection. The normal paraffin hydrocarbons of the general composition C_nH_{2n+2} consist of a chain of the composition $(CH_2)_n$, to each end of which one hydrogen atom is attached; in accordance with the principles already indicated, a close-packed assemblage of the empirical composition CH_2 can be constructed from carbon and hydrogen spheres of the respective volumes 4 and 1, of such a nature that it can be divided by planes

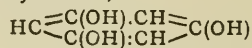
into blocks, each made up of strings of the composition $(CH_{2n})_n$, or $.CH_2.CH_2 \dots CH_2.CH_2.$ At each plane of cleavage of the assemblage hydrogen spheres can be inserted in appropriate numbers so that close-packing is restored when the cleavage faces are brought together again; the assemblage will then have the composition $H.(CH_2)_n.H$, and may be geometrically partitioned into units each representing one molecular complex of a normal paraffin. It is noteworthy that these units exhibit the configurations indicated by the van't Hoff-Le Bel conception for the normal paraffins. Other assemblages can be constructed which represent in a similar manner the secondary and tertiary paraffins, and all these assemblages are of one particular geometrical type, that which corresponds to the chemical behaviour characteristic of the paraffins. In these assemblages replacements may be effected so as to introduce new geometrical features of arrangement corresponding to the presence in the molecule of an ethylenic or an acetylenic bond, and thus other classes of hydrocarbons can be represented in accordance with the conception of close-packing; the process can be extended to the polymethylene and aromatic hydrocarbons and to their substitution derivatives, and throughout a close correspondence is observed between the numbers of isomerides possible, with their constitutions and configurations, and the experimental facts.

Many considerations indicate the fruitfulness of the mode of regarding organic substances just briefly sketched; one may be more particularly specified. An assemblage representative of benzene has been suggested which accords with the crystalline form and chemical properties of the hydrocarbon, and can be geometrically partitioned into units, each representing a single molecule. The equivalence parameters of the substance are $x:y:z=3:101:3,480:2,780$. The dimension y is twice the diameter of a carbon sphere, and that of z slightly less than the sum of the diameters of a carbon and a hydrogen sphere. Now a dimension approximating closely to the z value for benzene can be found amongst the equivalence parameters of large numbers of aromatic compounds, indicating that in these crystalline substances the benzene complexes are stacked one upon the other so as to preserve the z dimension, but that the columns so formed are pushed apart in the derivatives to an extent sufficient to admit of the entrance, in close-packing of the substituting radicles. A few cases of this kind were quoted by Barlow and myself, and many others were discovered by Jerusalem (*Trans. Chem. Soc.*, 1909, xcv., 1275); quite recently the subject has been subjected to a very thorough quantitative examination by Armstrong, Colgate, and Rodd (*Trans. Chem. Soc.*, 1910, xcvi., 1578; *Proc. Roy. Soc., A*, 1912, lxxxvii., 204; 1913, lxxxix., 292; 1914, xc., 111). The exhaustive nature of the experimental work of these latter authors and the care with which their conclusions are drawn leave little room for doubt as to the accuracy of their main contention, namely, that the crystallographic method affords material from which the stereochemical configurations of aromatic substances can be deduced.

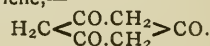
If crystallography is to be used as a tool in the service of stereochemistry in anything like the way which has been briefly sketched in this address, a number of important results should accrue. We have seen that in the structure assigned to rock-salt, each sodium atom is identically related to six chlorine atoms; only when the crystal is disintegrated by solution in water does the necessity arise for a choice to be made, the sodium atom then selecting one particular chlorine atom as a mate. Even then the sodium chloride molecule present in solution appears to spend the greater part of its time in dissociation, namely, in the act of changing its partner. There is thus in the theory of crystal structure something which bears a superficial relationship to electrolytic dissociation, and the further study of this aspect of the subject may be fruitful.

Again, the solid crystalline structures which we have attempted to build up present, as one essential feature,

the property that they can be partitioned geometrically into unit cells, each composed of one molecule of the substance; thus, the rock-salt structure can be partitioned into cells each representing the molecule $NaCl$. In this instance, the partitioning can be performed in a variety of ways corresponding to the allocation of one particular sodium atom to either of six chlorine atoms; the alternative modes of partitioning lead to the production of molecular units of identical configuration. In many cases, however, alternative methods of geometrically partitioning the assemblage representing the crystalline structure do not yield units of the same configuration; thus, the assemblage representing phloroglucinol can be geometrically partitioned in two distinct ways. Each of these gives a unit of the composition $C_6H_6O_3$, but the configuration of the unit of the one partitioning corresponds to the chemical structure of the 1:3:5-trihydroxybenzene,—



whilst the other exhibits the structure of the symmetrical triketohexamethylene,—



A new suggestion is thus made to the effect that tautomerism consists in the possibility of geometrically partitioning the close-packed assemblage in two or more alternative ways, each giving molecular units of the same composition but of different constitutions. The idea that in the occurrence of tautomerism some component atom wanders from one position to another in the molecule is thus rejected; the change in constitution arises from the transference of atoms as between two or more molecules. As the older conceptions of the mechanism of tautomerism do not provide a satisfactory explanation of the experimental facts, the suggestion now made is perhaps worthy of consideration.

The new line of work has many bearings upon the subject of chemical change; thus, the assemblage which is assigned to acetylene (or methylacetylene) is convertible, by symmetrical distortion, into that representing benzene (or the 1:3:5-trimethylbenzene, mesitylene). Further, the great change in chemical behaviour which accompanies many types of chemical substitution is possibly connected with the manner in which the actual atomic volumes are affected by the replacement; on converting benzene, in which the atomic volumes of carbon and hydrogen are as 4:1, into bromobenzene, a considerable increase in molecular volume occurs. The atomic volumes of carbon and hydrogen still, presumably, preserve the 4:1 ratio, and the volume appropriated by the entering bromine atom is approximately the same as that occupied by each hydrogen atom already present; the actual atomic volumes of carbon and hydrogen must thus be supposed to have increased during the production of bromobenzene. It can hardly be supposed that this fundamental volume change, even apart from a distortion of the aromatic ring arising from slight inequality of hydrogen and bromine atomic domains in the molecule, could occur without the exhibition of considerable differences in chemical properties as between benzene and bromobenzene.

Whatever view may be taken as to the accuracy of the conclusions concerning the relation between crystal structure and chemical constitution which are briefly discussed in the present Address, no critic will be disposed to doubt that wide developments in chemical science will result from the cultivation of crystal study; it seems clear that any satisfactory theory of the solid state must be largely crystallographic in character. The chief hindrance to progress at present consists in the lack of chemists trained in modern crystallographic methods; in my own country the only school in which chemical students were trained in Crystallography, dissociated from Mineralogy, was founded by Dr. Henry E. Armstrong and Sir Henry A. Miers in 1866. After doing a vast amount of valuable educational work this school has recently been allowed to become extinct.

In a Presidential Address to the Mineralogical Society in 1888, Mr. Lazarus Fletcher remarked that "a knowledge of the elements of Crystallography, including the mechanics of crystal measurements, ought to be made a *sine qua non* for a degree in Chemistry at every University." Twenty-five years later we find that no European University has applied this principle, and in consequence the chemical crystallographer has the greatest difficulty in making himself intelligible to his purely chemical colleagues. May I, in concluding, express the hope that the Colonial Universities, less fettered by tradition than their older sisters, may lead in the work of placing the subject of crystal structure in its legitimate position as one of the most important branches of modern Physical Chemistry?

ON THE SPECTRUM OF ELEMENTARY SILICON.*

By Sir WILLIAM CROOKES, O.M., Pres.R.S.

FEW elements have had so much attention directed to their spectra as silicon, and scarcely any element has shown such diverse results between recorded observations of different observers.

Hitherto no observer has recorded a complete table of lines from the shortest ultra-violet to the last pair of lines visible in the red. The values I now give are the result of observations extending over eleven years, during which time the advent of the colour-sensitive plate has made possible photographic records of lines that are visible.

The accurate tabulation of the wave-lengths of lines in the silicon spectrum is of considerable importance in physical astronomy; several stars, especially those of the Orion type, have lines corresponding to lines of silicon. Some years ago whilst studying the lines in a particular part of the silicon spectrum I was surprised to find that lines given by my own spectroscope did not altogether tally with lines in the same part of the spectrum recorded by other observers, some being altogether absent, while the wave-lengths of others did not correspond within allowable errors of observation. The cause of some of these discrepancies was traced to impurities in the samples of silicon used by myself and others. I endeavoured to clear up these doubtful points by trying to secure elementary silicon in as high a state of purity as possible. Every sample that could be obtained by purchase was tested and found to be far from pure, although impurities were different in kind as well as quantity.

Many different samples of fused silicon have been used by me in this research. Most samples were obtained by purchase from dealers in chemicals, rare metals, and their alloys. I could not find a sample sufficiently free from metallic impurity to show no extraneous lines in the spectrum. Some samples gave an excess of one set of lines, while others would give a number of lines due to another impurity. It was evident that all commercial silicon was impure, and the impurities in some samples were different from those in others. At first I started getting the lines actually due to silicon by enlarging the photographed spectra and then comparing the lines they had in common. In this way I got at last a tolerably good map of the silicon lines, which map, however, differed seriously from many maps given by other observers.

The Carborundum Company at Niagara Falls have been making large pans, cylinders, and vessels of fused and cast silicon for the use of manufacturing chemists. I wrote to the Niagara firm explaining my difficulties, and asking for silicon of a high degree of purity. They courteously replied that it was not possible to manufacture silicon in commercial quantities of a higher degree of purity than 98 per cent, but occasionally they got small specimens occluded in slags assaying 99 per cent and over. They

sent me three samples having this origin, giving on analysis 99.56, 99.86, and 99.98 per cent of silicon, the impurities being titanium, iron, and aluminium. These samples have been used in correcting the lines given by other less pure samples, and in clearing up doubtful points where impurity would interfere with certainty of identification.

Fused silicon is an interesting material, and when pure takes a high polish. Used as electrodes with the high frequency current much trouble is caused owing to a coating of oxide that forms almost at once, the spark becoming much less luminous. Under these conditions the surface of the electrodes presents a curious pitted appearance, as shown in Fig. 1. After trying many methods for keeping the spark bright, success was achieved by frequently removing the poles and grinding the surfaces with an emery wheel; in some cases where an exposure of seven hours was given a second pair of electrodes was employed, changing every fifteen minutes, and re-grinding one pair while the others were sparking.

The instrument used for measuring the lines is that described in my paper "On the Ultra-violet Spectrum of Radium" (*Roy. Soc. Proc.*, lxxii., 295). In most cases



FIG. 1.

pure iron was used to obtain the standard lines for comparison. Self-induction was introduced by an adjustable coil interposed in the path of the secondary current so as to suppress most of the air lines. The standard lines of iron or other metal selected for comparison with the silicon lines were photographed simultaneously on the same film, so that measurements could be taken in the comparator. From data so obtained the wave-length of each line was calculated by my son—Bernard H. Crookes, M.Sc.—according to the method given in my paper "On the Ultra-violet Spectrum of Radium" (*loc. cit.*, p. 302).

Recently an improvement has been made in my spectrograph, due to difficulties met with in photographing some of the very faint lines in the silicon spectrum. Long exposures were often necessary, in some cases many hours, and it was found that the variation in the temperature of the laboratory caused sufficient shift in the spectrum to make an otherwise sharp line appear blurred. With my

* A Paper read before the Royal Society, June 25, 1914.

WAVE-LENGTHS OF THE LINES IN THE VISIBLE PART OF THE SPECTRUM OF SILICON.

Rowland. 1898.	Lockyer. 1900.	Exner and Haschek. 1902.	De Gramont. 1903.	Lunt. 1905.	Frost and Brown. 1905.	Eder and Valenta. 1911	Crookes. 1914.	Remarks.
—	3853.9	3853.62	—	—	—	—	Pure elementary silicon.	
—	—	3854.02	—	—	—	3854.00	3853.812	This is a well defined group of one sharp line followed by two broad nebulous bands. The first of these bands at 3856.103 is the strongest. I find no evidence on any of my photographs of the line given by Exner and Haschek at 3853.62. My line at 3853.812 is certainly not a double one. The line given by Exner and Haschek at 3883.46 is not shown on my photographs, and Lunt (<i>Roy. Soc. Proc.</i> , lxxvi., 122) regards it as an impurity.
—	3856.1	3856.19	3856.0	—	—	3856.20	3856.193	
—	3862.7	3862.80	3862.5	—	—	3862.75	3862.743	
—	—	3883.46	—	—	—	—	—	
3905.660	3905.8	3905.71	3905.5	—	—	3905.80	3905.726	
—	—	4021.0	—	—	—	—	—	
—	4030.0	4030.1	—	—	—	—	—	
—	4089.1	—	—	4089.0	—	—	4089.016	
—	4096.9	4096.8	—	—	—	—	4097.021	
4103.007	4103.2	4103.2	—	—	—	—	—	I can find no evidence of either of these three lines on my photographs.
—	4103.7	4103.7	—	—	—	—	—	
—	4116.4	—	—	4116.0	—	—	—	
—	4128.1	4128.1	4128.0	4128.0	—	4128.2	4128.189	
—	4131.1	4131.0	4131.0	4131.0	—	4131.0	4131.192	
—	—	—	—	4191.0	—	—	—	Lunt gives these as a pair of "new silicon lines" (<i>Roy. Soc. Proc.</i> , lxxvii., 125). I find no trace of them on my photographs.
—	—	—	—	4198.0	—	—	—	
—	4552.8	4552.75	4552.5	4553.0	4552.64	—	4552.841	
—	4568.0	4567.95	4567.0	4568.0	4567.90	—	4568.123	
—	4574.9	4574.9	4574.5	4575.0	4574.79	—	4574.823	
—	—	4764.20	—	—	—	—	—	I cannot see a trace of a line near 4764.20 on my photographs.
—	5042	—	5045.5	—	—	—	5042.715	
—	5057	—	5059.8	—	—	—	5057.832	
5645.830	—	—	—	—	—	—	—	This group of seven lines is ascribed by Rowland to silicon, but I find no trace of them on my photographs.
5665.775	—	—	—	—	—	—	—	
5684.710	—	—	—	—	—	—	—	
5690.646	—	—	—	—	—	—	—	
5701.323	—	—	—	—	—	—	—	
5708.622	—	—	—	—	—	—	—	
5772.364	—	—	—	—	—	—	—	
5948.765	—	—	5960	—	—	—	5961.6	These two lines are faint and very nebulous. They were measured by means of the recording instrument described in this paper.
—	—	—	5879	—	—	—	5982.0	
6342.2*	—	—	6342	—	—	—	—	
—	—	—	—	—	—	—	6346.962	These are a pair of strong lines in the red. They were measured from photographs taken on Panchromatic films, giving seven hours' exposure.
6369.7*	—	—	6370	—	—	—	6371.032	

* These two lines are ascribed to Rowland by Dr. Marshall Watts, Appendix U, p. 4.

SILICON SPECTRUM. LINES IN THE ULTRA-VIOLET PORTION.

Rowland. 1893.	Hartley. 1901.	Exner and Haschek. 1902.	De Gramont and C. de Watteville. 1903.	De Gramont and C. de Watteville. 1908.	older and Valenta. 1911.	Crookes. 1914.	Remarks.
—	—	—	—	—	1929.0	Pure elementary silicon.	This is beyond range of my spectrograph.
—	—	—	—	2123.0	2122.8	2124.163	
2208.060	—	2208.1	—	2208.8	2208.1	2208.048	
2210.939	—	2210.97	—	2211.0	2210.9	2210.087	
2211.759	—	2211.84	—	2212.0	2211.8	2211.839	
2216.760	—	2216.75	—	2217.2	2216.76	2216.882	
2218.146	—	—	—	2218.7	—	2218.227	
—	—	—	—	2219.5	—	—	
—	—	—	—	2303.8	—	—	
2435.247	—	2435.22	—	2435.6	2435.25	2435.212	{ These two lines do not appear on my photographs. No observers but De Gramont and C. de Watteville have recorded them.
2438.864	—	2438.87	—	2439.4	2438.86	2438.911	
2443.460	—	2443.47	—	2443.5	2443.46	2443.484	
—	—	2443.91	—	—	—	—	{ These two lines do not appear on my photographs. They are only recorded by Exner and Haschek, and are recorded as of intensity (1).
—	—	2445.63	—	—	—	—	
2452.219	—	2452.23	—	2452.5	2452.22	2452.219	
2506.994	2506.8	2507.01	—	2506.8	2506.99	2507.055	
2514.417	2514.0	2514.41	—	2514.3	2514.42	2514.406	
2516.210	2515.9	2516.26	—	2516.0	2516.21	2516.131	
2519.297	2518.9	2519.30	—	2519.2	2519.30	2519.276	
2524.206	2523.9	2524.21	—	2524.3	2524.21	2524.110	
2528.599	2528.6	2528.60	—	2529.0	2528.60	2528.585	
—	—	2532.45	—	2533.0	—	—	
—	—	—	—	2535.0	—	—	No trace of a line is shown on my photographs near this spot.
—	—	2541.90	—	—	2541.89	2541.970	
—	—	2568.85	—	—	—	—	
2631.392	2631.8	2631.38	—	—	2631.39	2631.370	
—	—	—	—	2560.0	—	—	
2881.695	2881.5	2881.73	—	2881.7	2881.70	2881.690	
2987.766	—	2987.77	—	2987.8	2987.77	2987.750	
—	—	3086.6	3087.2	—	—	3086.479	
—	—	3093.6	3094.5	—	—	3093.604	
—	—	—	—	—	—	3247.84	
—	—	—	—	—	—	3438.444	
—	—	3591.0	—	—	—	—	
—	—	3791.8	3791.5	—	3791.1	—	
—	—	3796.50	3796.0	—	3795.9	3796.364	
—	—	3806.90	3807.0	—	—	3806.802	
—	—	—	3835.0	—	—	—	

* On examining my photographs under high magnifying power very faint lines can be seen in about these positions, but they are too faint to admit of trustworthy measurement.

There is no trace of a line here on my photographs.

original plan of projecting the two spectra upon the plate in succession by means of stops placed before the slit the temperature variation introduced inaccuracy; because the standard spectrum of iron or other metal only needed comparatively short exposure, and the room temperature during that period might be different to the mean temperature during the long silicon exposure.

To remove this uncertainty a right-angled quartz reflecting prism is mounted so as to cover the lower half

light from the brighter spark is reduced so as to equal the fainter one and make the resulting spectra of the same intensity.

The same end may be gained by giving one half of the exposure necessary for the brighter spark at the commencement, and one-half at the finish. For example, in the case of a seven hours' exposure of silicon, with a vanadium standard that needs only one hour, the exposure is made by starting both sparks simultaneously, and after thirty

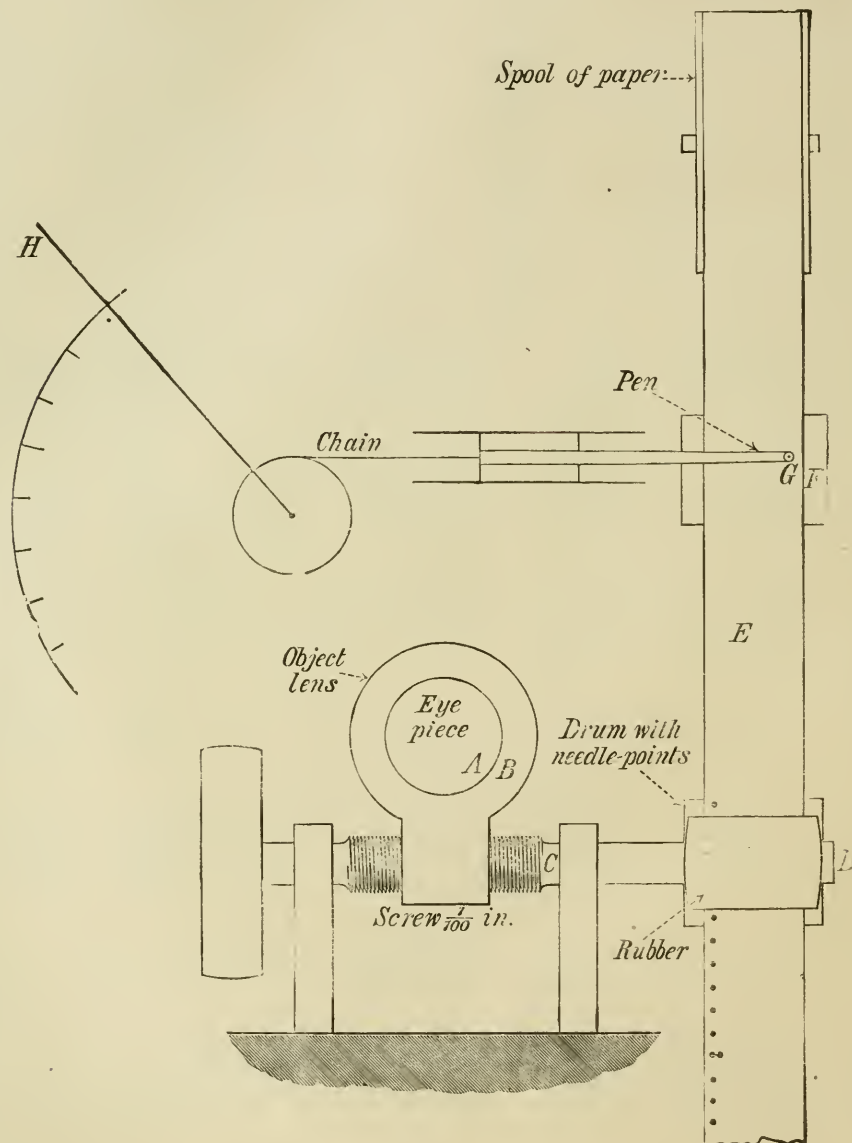


FIG. 2.

of the slit. The upper half of the slit receives the direct light from the sparking silicon, whilst the light from the standard metal spark is at the side, and is passed into the lower half of the slit by reflection through the right-angled prism. In this way both the standard and the silicon spark can be photographed simultaneously. The difficulty introduced by the varying brightness of the two sparks is avoided by adjustable diaphragms mounted between each spark and the slit; by adjusting these, the

minutes stopping the vanadium and starting it again after six hours and allowing both to finish together.

In this way any shift of the spectrum due to change of temperature results in an apparent broadening of the lines, and both the standard and the silicon are affected in the same way. The result on the photographic films is shown by two lines of spectra, running parallel to one another and almost, if not quite, touching. In the case of silicon, lines are met in the whole length of the spectrum from high

in the ultra-violet through the visible part to the red rays, and it happens occasionally that lines are present where an almost blank space occurs in the iron spectrum; in these cases some other element has to be selected containing spectrum lines in the desired gap. Some of the standard lines chosen have not been measured as accurately as those of iron; therefore my measurements based on such lines have not the same degree of accuracy as the lines measured against an iron standard. In some cases, however, I have been able to re-standardise the lines in the silicon used, by measuring them against iron lines near enough for this purpose, but not near enough to the silicon lines.

There are two lines of silicon in the orange-red portion of the spectrum, extremely faint and hazy in appearance; to get their image with the most sensitive panchromatic films required an exposure of many hours with the 5-prism quartz train. I therefore used for these lines an instrument designed some years ago whereby eye observations could be taken and recorded with the 5-prism spectrograph.

The apparatus shown in outline drawing, Fig. 2, takes the place usually occupied by the camera in the 5-prism spectrograph. It consists essentially of a telescope, AB, furnished with the usual micrometer eyepiece, A, and fine wires. The object lens, B, is mounted on an accurately cut screw, C, of one-hundredth of an inch pitch; by rotating the screw the lens B is moved sideways so as to traverse the spectrum over the wires in the eyepiece A; the prolongation of the screw C carries a brass drum, D, 1 inch in diameter, which has ten needle points equally spaced round it. A narrow roll of paper, E, is mounted on a spool just above the drum D, and one end of the paper is pressed on its surface by a soft rubber roller, F. Rotating the drum D therefore draws the paper off the spool E, and imprints on it ten perforations for each revolution of the drum. As one revolution of drum carries the object glass one-hundredth of an inch sideways across the lines under measurement, and the drum is 1 inch in diameter, the space between each perforation equals $1/1000$ th of an inch movement of the object glass. (The actual distance apart of the dots on the paper is 0.3146 of an inch). For convenience of calculation one of the needle points is doubled, so as to note each complete revolution. This device of marking the distances on the paper at the same moment as recording the lines eliminates any uncertainty that would otherwise be due to subsequent unequal alteration in the length of the paper.

The paper band, on its way from the spool E to the drum D, passes over a small table, F; at this point a fine pen, G, carried on a slide, can be made to trace a line any desired length across the strip of paper by pressure of the finger upon the lever H.

The method of measurement is as follows:—By rotating the screw, the spectrum is made to traverse the field of view, and when the line to be recorded coincides with the fine wires in the eyepiece, a touch of the finger on the lever, H, draws an ink record across the paper strip. When all the lines are recorded the paper strip is removed, and the distance between the dots on the paper can be subdivided into 10 parts by means of a transparent scale, by which the distance apart of any of the recorded lines can easily be measured. From these measurements the wave-lengths of the lines can be calculated in the same way as if the measurements were taken from a photograph. The distance apart of the sodium lines D_1 and D_2 , recorded on the paper strip, is 23 mm.

A good method of correcting these paper records is to take several observations upon each line in succession, moving the line backwards over the fine wire between each record. In the case of very sharp lines the records practically are in the same place. In other cases the ink lines may not be exactly superposed, because the lines to be measured are faint and hazy, and differences in position of the records are due to the almost insuperable difficulty of the eye hitting on the exact centre of the nebulousity.

In such cases accuracy is obtained by taking the mean of the adjacent records of the same line.

The first published record of the silicon spectrum is by G. Salet in 1873, who gave the wave-lengths of nine lines in the visible part of the spectrum from the orange to violet (*Ann. de Chim. et de Phys.*, xxvii., 65). His numbers differ from those of later observers, and as there are more accurate determinations of wave-lengths, I have omitted them as of no present value.

In 1893 and 1898 Rowland published the wave-length of 30 lines occurring in the solar spectrum, ascribed by him to silicon ("A Preliminary Table of Solar Spectrum Wave-lengths," Chicago; "A New Table of Standard Wave-lengths," *Phil. Trans.*, xxxvi., 49).

In 1900 Sir Norman Lockyer gave the wave-lengths of 14 lines in the blue part of the spectrum (*Roy. Soc. Proc.*, lxxvii., 403). He used silicon bromide in a vacuum tube and elementary silicon.

In 1901 Sir Walter Noel Hartley gave the wave-lengths of eight lines photographically recorded in the ultra-violet part of the spectrum (*Roy. Soc. Proc.*, lviii., 179; this paper is a revision, as far as the wave-lengths are concerned, of measurements of the lines published by the same observer in 1883). He obtained them by saturating one of the carbon poles with sodium silicate.

In 1902 Exner and Haschek published a list of 45 wave-lengths of lines in the silicon spectrum from the extreme ultra-violet to the blue ("Wellenlangen-Tabellen für Spektral-analytische Untersuchungen," Leipzig and Wien).

In 1903 A. de Gramont, using elementary silicon and sodium silicate on platinum wire, gave a list of silicon lines partly selected for astronomical comparisons (*CHEMICAL NEWS*, lxxxviii., 238; a paper read before the British Association, Southport Meeting).

In 1905 J. Lunt gave a list of nine lines of silicon, in the blue portion of the spectrum (*Roy. Soc. Proc.*, lxxvi., 118). These were seen in various vacuum tubes.

In the same year E. B. Frost and J. A. Brown, using elementary silicon and titanium prepared in the electric furnace, made careful measurements of three silicon lines selected as being of especial utility in determinations of the radial velocity of numerous stars (*Astrophys. Journ.*, xxii., 157, 260).

In 1908 de Gramont, in conjunction with C. de Wetteville, using silicon poles in an atmosphere of hydrogen, published a further list of 23 lines ranging from the extreme ultra-violet to the point in the violet where de Gramont's earlier list commenced (*Comptes Rendus*, cxlvii., 239).

In 1911 Eder and Valenta published a list of 28 lines in the silicon spectrum, mostly in the ultra-violet portion and extending down to the blue ("Atlas Typischer Spectrum," Wien).

In the accompanying Tables I give the wave-lengths of the silicon lines measured by the observers named above. Earlier spectrum observations were necessarily imperfect, chiefly because of the difficulty in getting elementary silicon even in an approximate state of purity. Some observers also have limited the range of their observations to a small part of the spectrum, for astronomical and other reasons.

Liberation of Nitrogen in the Reaction of NaOBr on Urea.—C. Alberto Garcia.—The author finds that with his nitrometer he always gets values very closely approximating to the theoretical values for the nitrogen in urea, even with solutions of different concentrations. This he attributes to the fact that he works *in vacuo*, and it appears that when the gas liberated by a reaction is determined in presence of substances in solution, the operation should always be performed *in vacuo*. Otherwise the liberation of gas is not complete, for some always remains dissolved in the solvent.—*Bull. Soc. Chim. de France*, xv.-xvi., No. 12.

SYNTHETIC RESINS.*

By L. V. REDMAN, A. J. WEITH, and F. P. BROCK.

(Continued from p. 76).

Combustion Analysis of the End Product Formed in Excess Phenol.

THE analysis of a resin which we have prepared by boiling a mixture of 12 mols. of dry phenol and 1 mol. of hexamethylenetetramine until all the nitrogen has been evolved as ammonia, dissolving the resulting thick, yellow liquid in 5 per cent KOH and precipitating with 2NHCl, the precipitate filtered off into Norton cones and washed with 2NHCl and dried at 50° C. in a gas oven, gave results as follows:—

Calculated for C ₁₀₄ H ₉₂ O ₁₆ . Per cent.	Found.		Calculated for C ₉₀ H ₈₀ O ₁₄ . Per cent.
	Per cent.	Per cent.	
C = 78·16	C = 77·98	77·96	C = 78·04
H = 5·81	H = 6·17	6·23	H = 5·88
O = 16·03	O = 15·85	15·81	O = 16·16

1. C₁₀₄H₉₂O₁₆ may be written 14(C₇H₆O).C₆H₅.O.H₂O.
2. C₉₀H₈₀O₁₄ may be written 12(C₇H₆O).C₆H₅.O.H₂O or C₆H₅.OCH₂.C₆H₄.OCH₂.C₆H₄.OCH₂.C₆H₄OH.

Dr. Baekeland's published analyses of certain soluble products which he has obtained by heating excess phenol in the presence of formaldehyde solution (L. H. Baekeland, *Journ. Ind. and Eng. Chem.*, 1909, i., 545) and by heating oxybenzyl alcohol and phenol are as follows:—

Calculated for C ₁₀₄ H ₉₂ O ₁₆ . Per cent.	Found for Phenol + CH ₂ O.		Found for Saligenin + Phenol.	
	Per cent.	Per cent.	Per cent.	Per cent.
C = 78·16	78·04	77·95	78·16	78·24
H = 5·81	5·79	5·97	5·65	5·75
O = 16·03	16·17	16·08	16·19	16·01

That the end of the molecular chain in the individual, made as described above, cannot have a CH₂OH group attached to the benzene ring is evident from the fact that the reaction between anhydrous phenol and hexamethylenetetramine could not produce such a substance, especially since, as will be shown presently, the only by-product from the reaction is ammonia. The other end of the molecule is hydroxylated, probably, as the substance is readily soluble in alkalis.

The H₂O may be either a water of hydration which attached itself to the molecule during the process of solution and precipitation, or, which seems more reasonable, the process is one of oxidation, for the individual changes its colour from yellow to green when it dissolves in alkali and from green to red when it is precipitated by acid. The drying of the pptd. material at 50° C. changes the colour further to a reddish brown. This possible oxidation is described at further length (see *prox.*). Such a formula would have a molecular weight for C₁₀₄H₉₂O₁₆ = 1552 or for C₉₀H₈₀O₁₄ = 1384. The highest formula weight calculated from the rise in boiling-point which Dr. Baekeland has found for novolak dissolved in acetic acid is 1216 (*Journ. Indust. and Eng. Chem.*, 1909, i., 545).

Aylesworth (Brit. Pat. 4396, 1911) in his U.S. patent 1,029,737 lays claim to the production of a soluble phenolic resin formed from phenol and formaldehyde by boiling 2 mols. of phenol in 1 mol. of aqueous formaldehyde until a resin is produced having the formula C₆H₅.OCH₂.C₆H₄.OCH₂.C₆H₄OH (H. Lebach, *Journ. Soc. Chem. Ind.*, 1913, xxxii., 561) as shown by boiling-point analysis. This is quite impossible for the reason that such a resin is not an individual but may be dissolved up in KOH and separated into two constituents by the addition of HCl, the precipitate containing approximately 50 per cent and the filtrate holding in solution approximately

50 per cent of the original phenol used. The rise in the boiling-point given by Aylesworth is no doubt caused by the 50 per cent free phenol and shows that the molecule of the resin is so large in the precipitate as to have very little effect upon the boiling-point of the solvent employed, as the rise in the boiling-point may be accounted for by the free phenol present.

A further proof that the molecule consisting of 12 methylenes and 13 phenols is from the fact that the total amount of resin formed in a phenol solution, and which is precipitated by the acid as described above, corresponds in weight to 6½ phenols to each 6 methylenes added or 13 phenols to 12 methylenes. This is in agreement with the combustion analysis, and with the highest number obtained in the rise of boiling-points. The formula then which we propose for this soluble resin is—



and following Kraut's suggested nomenclature we have called this material phenyl-endeke-saligeno-saligenin (*Ann. der Chem.*, clvi., 123).

That this resin is an intermediate product which later is transformed by being mixed with formaldehyde or hexamethylenetetramine and heated into the insoluble infusible methylene phenol condensation products of the highest dielectric and tensile strength and chemical inertness, is almost certain from the fact that an aggregate can be made consisting of 10 mols. of phenol to 1 mol. of hexamethylenetetramine and this heated until all the ammonia has been evolved, which results in a heavy, viscous yellow transparent liquid when hot and semi-solid when cold, consisting of over 63 per cent phenyl-endeke-saligeno-saligenin (novolak), the rest being water-soluble phenols; hexamethylenetetramine is then added in such proportions as to make the total phenol to methylene in the ratio of 1 : 1 and heated until the mass has become a yellow porous sponge, the mass is then powdered and pressed in moulds at 200° C. and 12,000 lbs. per sq. in. for 5—10 mins. and the resin becomes a transparent amber-like material with a dielectric strength of 50—90,000 volts. per mm., an ohmic resistance of 2 × 10⁹ per cm³. and a tensile strength of 4000—4500 lbs. per sq. inch.

That a substance consisting of more than 60 per cent phenyl-endeke-saligeno-saligenin and the remainder a water-soluble phenol is transformed by the addition of hexamethylenetetramine and further heating into an insoluble substance of such high dielectric and tensile strength, seems to preclude the possibility of this resin remaining unchanged or transforming into any other product than an insoluble infusible resin of highest dielectric and tensile strength. For it must be remembered that this resin, of itself, is more brittle than cheap rosin and soluble in all the ordinary solvents.

Indeed we have found this intermediate substance present in all the materials we have made of whatever variety, soluble or insoluble, whether heated for a long or short period and whether at a high or relatively low temperature. Low temperature, a short time of heating, and excess phenol, or what is the same thing, not enough hexamethylenetetramine to make a 6 mols. of phenol to 1 mol. of hexamethylenetetramine resin gives a greater percentage of this soluble resin. It is also present in small proportions in 6 : 1 resins that have been heated for many hours at 200° C.

Table I. gives the result of a few analyses of resins as described.

When the soluble, brittle, fusible resin is mixed, powdered, and heated for one hour with hexamethylenetetramine in the proportions of 6 mols. of novolak to 1 mol. of hexamethylenetetramine, assuming 1 mol. of novolak, C₉₀H₈₀O₁₄ = 1384, the mass becomes largely insoluble in all ordinary solvents, caustic alkalis, &c. It swells or gelatinises in boiling phenol but does not dissolve and exhibits generally the properties of the insoluble products. The final resin formed from the novolak and hexamethylenetetramine is much darker than the

* *Journal of Industrial and Engineering Chemistry*, vi., No. 1.

TABLE I.

Resin and how made.	Original proportion of phenol to methylene.	Per cent of material insoluble in KOH.	Per cent of free phenol.	Per cent of phenylene-deka-saligeno-saligenin.
Dry phenol and hexamethylenetetramine, heated on a water-bath fourteen hours, later heated in an air-bath at 100° C. for 221 hours	8 : 6	68.4	8.9	22.7
A Bakelite pipe stem bought in the market	?	94.4	—	4.2
Bakelite lacquer No. 5, satin finish (a)	?	94.0	—	3.2
6 : 1 resin heated fifteen hours at 125° C. (c)	6 : 6	80.0	32.5 (b)	52.1
6 : 1 resin, containing 7 per cent naphthalene, heated ten hours at 122° C.	6 : 6	68.4	1.0	20.0
6 : 1 resin heated later in mould for one hour	6 : 6	84.7	6.3	19.5
6 : 1 resin heated for five hours at 154° C.	6 : 6	90.0	1.3	18.7
			1.96	7.64

(a) The lacquer was 22 per cent resin and 78 per cent solvent. The percentages in the table are calculated on the resin.
 (b) This is doubtful, as the figure was obtained by the regular bromination method and the results calculated for free phenol. The real values are probably higher.
 (c) 6 : 1 resin is formed by heating together 6 mols. phenol and 1 mol. hexamethylenetetramine.

resin formed directly from phenol and hexamethylenetetramine. This is, no doubt, due to darkening which takes place when the resin is separated from the excess free phenol.

(To be continued).

NOTICES OF BOOKS.

Alcoholic Fermentation. By ARTHUR HARDEN, Ph.D., D.Sc., F.R.S. Second Edition. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1914.

In the second edition of this book no change has been made in its scope or plan, but some additions to the text have been found necessary. For instance, Euler's investigation of the mechanism of the formation of hexose diphosphoric acid is fully discussed, recent work on carboxylase is described, and the study of the chemical changes involved in fermentation by Kostytscheff and others is obtained. The bibliography has also been considerably extended.

The Preparation and Commercial Uses of Hydrogen. By ARTHUR W. CROSSLEY, D.Sc., Ph.D., F.R.S. London: St. Clements Press, Ltd.

This lecture, which was delivered before the Pharmaceutical Society in April, deals very comprehensively with a highly important subject. Methods of preparing hydrogen upon the large scale are discussed, selection having been carefully made from among the many hundreds of patents which have been taken out during the last few years. The two new industries depending upon catalytic hydrogenations which have recently sprung up, viz., the synthesis of ammonia from atmospheric nitrogen and the hardening of fats are very clearly treated, the researches of Sabatier and Senderens and others being first described. The great possibilities of both processes are pointed out, and it seems likely that hardened oils will be largely used in the future both for lubricating purposes and for food-stuffs.

Les Gaz Rares des Grisons. ("The Rare Gases in Fire Damps.") By CHARLES MOUREU and ADOLPHE LEPAPE. Paris: H. Dunod and E. Pinat. 1914.

THIS pamphlet contains an account of the authors' investigation of the constituents of specimens of fire-damp from various sources. The experimental methods adopted are fully described in the first chapter, and details are given of the burning, in the absence of air, of the fire-damp and the preparation of raw nitrogen (nitrogen + rare gases). The numerical results obtained are given in full, and some notes are added on the composition of fire-damp and similar natural gaseous mixtures, and on the constancy of certain volume relations, such as that of krypton to argon, xenon to argon, &c. The authors infer from their observations that all natural nitrogen is of the same origin, dating from the nebular epoch.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 25, June 22, 1914.

Reduction of Carbon Monoxide by Hydrogen induced by Radium Emanation.—Otto Scheuer.—Under the action of radium emanation CO is reduced by hydrogen, and gives first of all HCHO, which is then completely reduced to methane, which is the principal ultimate product of the reaction. Some proportions of other hydrocarbons are also formed. The intermediate formation of methyl alcohol has not been observed in these experiments, although it seems probable. All these reactions are accompanied by the production of water.

Allylcyclohexanones and Methylallylcyclohexanones.—R. Cornubert.—The author has prepared and studied the allylcyclohexanones obtained from cyclohexanone and its α , β , and γ methyl derivatives. These four ketones gave all the derivatives theoretically possible; allylation while always easy becomes less so as it is more advanced. The saturated allyl derivatives are obtained with the theoretical yield. The mono allyl derivatives all have a smell of mint and give oximes; the yield of them is better the nearer the methyl group is to the carbonyl.

Transformation of Barbaloin into β -Barbaloin.—E. Léger.—If a mixture of acetic anhydride, barbaloin, and sodium acetate is heated to 100° to 110° for an hour a yellow liquid is obtained which gives a yellow precipitate with a large quantity of water. This product has the formula $C_{20}H_{13}(C_2H_5O)_5O_9$, and is a pentacetylbarbaloin. When it is saponified it gives barbaloin and also β -barbaloin.

Bulletin de la Société Chimique de France.
Vol. xv., xvi., No. 12, 1914.

Solvents of Coal.—Léo Vignon.—Aniline can be used to differentiate chemically coals known technically as fat, semi-fat, and thin. The first contain relatively large quantities of substances soluble in aniline and the last comparatively little. These substances, which are soluble in aniline, are precipitated by acids. If the insoluble portions and the substances precipitated in their solution are compared, it is found that the soluble portion is richer in hydrogen and poorer in ash. Boiling quinoline extracts a considerable quantity of material from fat coals.

Ethers of Choline.—E. Fourneau and Harold J. Page.—The authors have prepared the chlorides, iodides, and bromides of several ethers of choline by heating the ethers of chloroethanol, iodoethanol, or bromoethanol with trimethylamine in benzene solution. As derivatives

of choline these ethers give characteristic crystalline precipitates with picric acid, platinum chloride, and gold chloride. With iodine solution they give an oily precipitate and not the Florence reaction which is so characteristic of choline. The concentrated aqueous solutions of the higher members of the series do not precipitate silver nitrate, but give a colloidal solution. The ether function is easily saponified. The chlorides are much more stable than the iodides and are not altered in alcoholic solution, while the latter are more or less rapidly hydrolysed when boiled with alcohol. In neutral aqueous solution the ethers are at once saponified by soda, but they are fairly stable in presence of sodium carbonate. They are equally stable in acid solution in the cold, but are rapidly hydrolysed on warming. The aqueous solutions themselves can be boiled without undergoing alteration, but if the boiling is continued for too long they are slowly decomposed and the liquid becomes acid.

Analysis of Essential Oils.—A. Béhal.—In determining the ether salts in essential oils it is often found that even with the same essence in identical conditions the results differ by as much as 3 per cent. The author has investigated the cause of this error, and finds that it is due to a new reaction. The ether salts are decomposed in presence of alkalis and alcohols to give a certain amount of ether salt corresponding to the alcohol of lowest molecular weight, the alcohol of highest molecular weight being liberated.

Atti della Reale Accademia dei Lincei.

Vol. xliii. [i.], No. 9, 1914.

Asymmetrical 1.2.4-Trinitrobenzene.—G. Koerner.—The author has prepared the nitrate of the diazo compound of ordinary dinitroaniline fusing at 180°, and then treated it with solutions of copper sulphate and sodium nitrite and extracted with chloroform. The trinitrobenzene thus obtained consists of almost colourless crystals melting at 61°. When heated in closed tubes to 140° with alcoholic ammonia it is transformed quantitatively into the original dinitroaniline.

Phenomena of Transformation of Sodium Molybdate and Tungstate.—M. Amadori.—In the author's experiments the solidification point of sodium molybdate was found to be 688°. The first two points of transformation occur at 616° and 580° and the third at 410°; the transformation takes place accompanied by the development of a considerable amount of heat. Sodium tungstate solidifies at 696°, and the temperatures of transformation are 582° and 571°.

MISCELLANEOUS.

Iron and Steel Institute.—In consequence of the war the Comité des Forges de France has been obliged to cancel all arrangements for an Autumn Meeting of the Institute in France this year. Under the circumstances, the Council has decided that it would be advisable to postpone for the present the organisation of any alternative arrangements for an Autumn Meeting for the reading and discussion of papers. A number of papers have been submitted with a view to their presentation at the meeting which was to have been held at Paris, and the Council proposes to print in the usual way advance copies of those papers approved for publication and to invite discussion thereon by correspondence. It is expected that the copies will be ready for issue about the second week in September. Members who desire to send in written communications in discussion of any of the papers can be supplied with copies of those in which they are interested on application to the Secretary. The papers and correspondence thereon will be published in the next number of the Journal. If, later in the year, any meeting becomes necessary for the discharge of formal business of the Institute, due notice

will be sent to all Members. A list of the papers is given below. The Council cannot let this occasion pass without placing on record an expression of their most sincere sympathy, which they are sure will be shared by all Members, with their President, M. Adolphe Greiner, and his family in the great anxieties under which they are at present suffering, in common with his countrymen, at whose hands the Institute experienced such kindly hospitality in the Autumn of last year. The following is the list of papers that have been submitted:—

- E. D. CAMPBELL—"Note on the Theory of Hardening and on the Constitution of Steel."
- G. S. COOPER—"By-product Coking Industry and its Relation to the Manufacture of Iron and Steel."
- L. DUFFY—"Determination of Cobalt in High-speed Steels."
- L. GUILLET—"Electrolytic Iron, its Manufacture, Properties, and Uses."
- G. HAILSTONE—"Transverse Testing of Cast Iron."
- W. L. JOHNSON—"Utilisation of Heat contained in Slags."
- N. G. CAPP—"Mechanical Charging of Blast-furnaces."
- P. NICOU—"Iron Ore Deposits of Lorraine and the West of France."
- H. de NOLLY and M. VEYRET—"The Transformations of Steels."
- J. A. PICKARD and F. M. POTTER—"Oxygen Content of Open-hearth Steel."
- A. M. PORTEVEN—"Decarburisation of the Steels in Salt Hardening Baths."
- A. M. PORTEVEN and V. BERNARD—"Influence of Coal-escence on Mechanical Properties of Steels and Alloys."
- A. SAHLIN—"Use of Liquid Ferro-manganese in the Steel Processes."
- A. SPANNAGEL—"New Process for Heating Blast-furnace Stoves."

Analysis of Radio-active Substances by Sublimation.—C. Ramsauer.—A relatively simple method of determining the proportions of radium, thorium, and actinium in active substances depends upon the sublimation of the active deposits accumulated in the substance upon a cooled surface; the curve of disactivation is then studied, regarded as the sum of the three fundamental curves which are calculated theoretically and verified by experiment. The experimental conditions are chosen in such a way as to make the three curves as characteristic and different as possible. (Temperature of calcination 1150°, duration of calcination four minutes, total duration five minutes). The activity obtained by sublimation is compared with that obtained by the emanation alone. This method has been applied to the analysis of the thermal mud of Kreuznach, which contains per ton:—1.75 mgrms. radium, 1.88×10^{-6} mgrms. thorium X, 4.80×10^{-6} actinium X.

NOTICE.

The STUDENTS' NUMBER of the CHEMICAL NEWS will be published on Friday, September 18th. Gentlemen holding official positions in the Universities, Medical Schools, &c., of the United Kingdom, where Chemistry and Physical Science form a part of the education, who have not yet forwarded the necessary information to our Office for publication in that Number, will confer a favour by sending it with the least possible delay.

Advertisements for this Number should reach the Advertisement Manager as early as possible, but not later than the first post on TUESDAY, SEPTEMBER 15. Reserved spaces or special positions will be booked according to priority of application.

THE CHEMICAL NEWS

VOL. CX., No. 2859.

ADDRESS TO THE ENGINEERING SECTION OF THE BRITISH ASSOCIATION.

AUSTRALIA, 1914.

By Prof. E. G. COKER, M.A., D.Sc., M.Inst.C.E.,
President of the Section.

THE subject of stress distribution in materials, which I have chosen for this Address, is not one which an engineer can claim as his peculiar province, for it has been and still is a fruitful field of investigation for the mathematician, the physicist, and the geologist, and has always been so since the commencement of scientific inquiry; indeed, it must have been the source of speculation and controversy ever since mankind emerged from a primitive state, and began to fashion dwellings, weapons, and tools from the materials at command.

The development of architecture from the earliest dwellings of savage races to the great temples of Egypt and Greece, the bridges and aqueducts of the Romans, and the mediæval buildings of Europe, all bear witness to the accumulation of practical knowledge of the properties of materials, and of the stress distribution in structures, which we cannot fail to admire, although we know far too little of the way in which these ancient structures were planned and constructed. The magnificent arched and domed buildings of the Roman period, and the stately cathedrals of later times with their wealth of architectural form—tower and spire, flying buttress and vaulting—all show how considerable was the practical knowledge of stress distribution possessed by the master builders who planned and carried out these great structures. We, who inherit these buildings as a precious legacy of bygone ages, have at our command far greater resources in the accumulated knowledge of centuries of scientific discovery and invention, and can build more complex structures—great bridges of steel, towering frame-works covered by a thin veneer of masonry, and floating arsenals of the most bewildering intricacy. All these we can show to our credit as the result of the steady increase of scientific knowledge applied to practical ends, but, even now, knowledge of the stresses which come upon these complex structures and machines is relatively small. Scientific investigations of engineering problems of stress still lag behind constructive ability, and defective knowledge is obscured more or less by approximate theories and buttressed by factors of safety, which serve in one instance perhaps, but show in others that they have merely given a sense of fancied security with no real basis, and are more properly factors of ignorance, to be discarded at the earliest moment. Who, for example, can say with certainty what is the stress distribution throughout the compression members of a great bridge, built up of complicated steel shapes and plates, united by stiffening angles, gusset plates, and innumerable rivets. There is probably good reason for the belief that a great strut is relatively weaker than a small one, when both are designed according to the same approximate formulæ now used in current practice, and engineers are unwilling to take the responsibility for such members in a great structure, without providing a very ample margin of safety to cover the contingencies arising from lack of precise knowledge of the strength of these members. So numerous are the problems which arise in the design and construction of machines and structures, that it is perhaps not unprofitable to devote a short hour to the consideration of some of the available means which an engineer can use as a guide for his application of

science to construction, since of whatever kind are the professional activities he pursues, his place in the scheme of affairs mainly depends on his ability to make machines and structures for directing and modifying natural sources of power in known ways, or applying them to new purposes as scientific discoveries advance the boundaries of knowledge.

The power to do this depends, to no small extent, upon the ability to determine the distribution of stress in a structure, and the skilful manner in which material can be disposed for the required purpose.

It is of some help to our appreciation of the achievements of the great constructors of past ages, if we remember that they probably all held the erroneous view that materials of construction are perfectly rigid bodies, and, indeed, we know that as late as 1638 Galileo Galilei was of that opinion, and that he came to an entirely wrong conclusion as regards the stress distribution in a loaded cantilever.

It required the genius and insight of Robert Hooke to make a really great step, with his celebrated theory of the linear relation of stress to strain, and we can appreciate the glow of pride and satisfaction which he must have felt at his great discovery, when he records in 1675 that "His Majesty was pleased to see the experiment that made out this theory tried at Whitehall, as also my spring watch."

Hooke had, in fact, discovered the fundamental principle upon which a theory of the elasticity and strength of materials could be based, and it would be interesting to trace the great advances which were rapidly made from this new vantage ground, whereby the main facts of the distribution of stress in simple members of structures became known, and a foundation was laid for the great advances of the mathematical theory. If I am silent upon the enormous developments of the modern theory of the strength of materials it is not from lack of appreciation, but because I do not deem myself adequately fitted to discuss the great work of the elasticians, which all engineers admire, and so few are equipped to follow with the full battery of mathematical tools which have been pressed into service in the pursuit of this great science.

Among the greatest of the services rendered by early pioneers was that of Young, who was the first to notice that the elastic resistance of a body to shear was different from its resistance to extension or contraction, and this led him to define a modulus of elasticity for materials in compression. As Professor Love remarks, "This introduction of a definite physical concept, which descends, as it were, from a clear sky on the readers of mathematical memoirs, marks an epoch in the history of the science."

From the standpoint of the engineer, nothing is of more practical importance than the great discoveries of Hooke and Young, that bodies like metal, wood, and stone are "springy" and have a simple linear relation between stress and strain. It is probably within the mark to say that nine-tenths of all the experimental investigations on stress distributions in structures have been entirely based on the fundamental principles which they enunciated, and new uses are continually arising. The recent application of the steam turbine to the propulsion of ships produced a profound change in marine-engine practice, and incidentally involved an entire reconstruction of methods for obtaining the horse-power developed, which had been gradually perfected from the time of Watt, but were absolutely useless for the new system of propulsion. Hooke's discovery of the essential springiness of metals enabled engineers quickly to devise new instruments capable of accurately measuring the infinitesimal angular distortions of propeller shafts, and from these to determine the horse-power transmitted by the aid of an appropriate modulus.

The construction of tall buildings affords another example where advantage has been taken to determine the loads upon columns by measuring the minute diminutions of length as the structure proceeds, thereby affording a

valuable check upon the calculations for these members, and a reliable indication of the pressures supported by the foundations.

The distribution of stress in buildings constructed of composite materials like concrete reinforced with steel has also been examined by similar methods, and much data for guidance in future constructional work has been obtained, especially in the United States of America.

The still more difficult problems involved in the determination of the stresses in joints and fastenings of complicated structures has often been investigated by purely mechanical measurements of strain, and the experimental investigations of Professors Barracough and Gibson and their pupils upon the distribution of stress due to riveted joints and curved plates of boiler shells afford a notable example of the successful application of the measurement of small strains to a stress problem of great complexity.

That "science is measurement" is here sufficiently obvious, and it seems only due to the memory of that great engineer, Sir Joseph Whitworth, to refer to his great mechanical achievements of a true plane and well-nigh perfect screw, which enabled him to measure changes of one-millionth of an inch, and thereby gave experimental investigations of strains a new impetus, which is reflected in subsequent work on the subject. Nor must we forget the no less important exposition, by Kelvin and Tait, of the scientific principles of instrument construction which have done so much for the design of instruments for the precise measurement of strains.

Mechanical measurements cannot, however, completely satisfy all our modern requirements, since they are essentially average values, and fail to accommodate themselves to many of the problems which press for solution.

In the quest for exact experimental knowledge, the measurement of stress at a point becomes of paramount importance, and we may therefore inquire what further means the researches of pure science have placed at our disposal for the determination of stress distribution in materials.

It is well known that many materials when tested to destruction show a considerable rise of temperature at the place of fracture, especially in very ductile materials; but Weher was the first to discover that a metal wire when stretched within the elastic limit is cooled by the action of the load, and this result was deduced later from the laws of thermo-elastic behaviour of materials by Lord Kelvin, who showed that tension and compression loads produce opposite effects, and that materials which have the property of contracting with rise of temperature show thermal effects of the reverse kind. Although the changes of temperature produced by stress are small within the elastic range—less than 1°C . for most materials—yet their effect upon a thermo-couple is readily measurable if the equilibrating effects of surrounding bodies are neutralised or allowed for, so that stress distribution can be determined by thermal measurements at a point. The correction for such disturbing causes is usually an important factor, and is generally so large that experimental work is more suitable for the laboratory than the workshop; but if all necessary precautions are taken a linear relation of stress to strain can be shown to hold up to the elastic limit of the material, while above this point the break-down of the structure causes a rise of temperature of so marked a character that it has been utilised by several investigators as an indication of the yield point.

Experiments upon members subjected to tension, compression, and bending, show that thermal phenomena afford trustworthy indications of the stress in materials so diverse as a rolled-steel section, a block of cement, and beams of stone and slate. Although no attempt appears to have been made to investigate stress distributions of any great complexity, it seems not unlikely that thermal methods of investigation will ultimately prove of considerable value.

The transparency of metals to Röntgen rays is another phenomenon which has often been suggested as likely to

be of service for work on stress distribution in materials, and Mr. Howgrave Graham and I have examined a number of rolled metals under stress up to the breaking point, without, however, discovering any change in the appearance of the material as seen on a fluorescent screen. Although our experiments showed no perceptible change, it is, of course, not impossible that an effect may have escaped our notice.

Another and still more fascinating field of research on stress distribution is afforded by the doubly refractive properties of transparent bodies under stress, a discovery made by Sir David Brewster almost exactly one hundred years ago, and but rarely made use of since by engineers, although Brewster himself immediately saw its value for experimental purposes, and suggested that models of arches might be made of glass, and the effects of stresses due to loading rendered visible in polarised light.

Brewster carried his investigations further, by the invention of a "chromatic teinometer" for investigating the nature of strains, and consisting of plates or bars of glass subjected to flexure in definite ways for comparison with the body under stress.

At a much later date (1841) Neumann developed an elaborate theory for the analysis of strain in transparent bodies due to load, unequal temperature, and set, while, still later, the youthful genius of Clerk-Maxwell supplied an algebraic solution for the stress distribution in any plate subjected to stresses in its own plane.

The early history of the development of this branch of science is, in fact, remarkable for notable contributions at long intervals of time, and the almost complete disregard by engineers of its practical importance.

The application of optical investigation to the determination of stress distribution in engineering structures and machines has, however, been hindered by causes which, although apparently insignificant, have been very real obstacles, and among these was the absence of a transparent material which could be fashioned into shapes suitable for investigating technical problems. It is not an easy matter, for example, to construct a glass model of a bridge free from internal stress, in the manner suggested by Brewster, and, moreover, glass is extremely fragile under load, especially in cases where the stress distribution in it varies very much, while the cost of construction is very great. Happily there is now no necessity to employ glass for experimental investigation on engineering problems, since modern chemistry has supplied artificial bodies, such as the nitro-cellulose compounds used for many trade purposes, which have optical properties very little inferior to glass, are able to bear great stresses without injury, and also are capable of being fashioned with the ease and certainty of a wooden model. Photographic processes are also able to reproduce the brilliant colour effects caused by stress in transparent materials, so that permanent records can now be made for future reference.

The construction of polariscopes for examining models on a large scale is very essential for technical research, and the great scarcity of Iceland spar of sufficient purity and size for use as Nicol's prisms has caused much attention to be paid to the construction of apparatus for producing plane polarised light by the aid of sheets of glass. Fortunately this presents little difficulty, and although the light is not nearly so well polarised as that obtained from a Nicol's prism it is sufficiently so for the purpose. Large quarter-wave plates of mica have also been constructed by my colleague, Professor Silvanus Thompson, F.R.S., for obtaining circularly polarised light, and these have proved sufficiently exact and exceedingly useful for large models.

It is of importance to show that the stress distribution revealed by a polarised beam of light passing through an elastic transparent material in no way differs from that obtained by other means, and evidence is available in modern researches, especially by Filon, that the experimental results obtained with glass agree with those of the theory of elasticity, while a satisfactory agreement of a similar kind has also been obtained with nitro-cellulose

compounds, although not in so complete and direct a manner. Such an agreement may be expected on the theoretical grounds, since the values of the elastic constants do not affect the fundamental equations for stresses in a plane, and although for three-dimensional stress the effect of the stretch-squeeze ratio causes some difference, yet this is usually negligible.

Most of the physical constants of glass have been determined with very considerable accuracy, but other transparent substances have so far received little attention, and their optical constants are not well known. The stress-strain relations of glass and nitro-cellulose have been determined with considerable accuracy, and a useful idea of their relation to metals may be gained from the values of the stretch-modulus, E , and the stretch-squeeze ratio, σ .

The accompanying table shows some average values for a few important materials, and it is of interest to note that the stretch-squeeze ratios of cast-iron and plate-glass are very similar, while the values of the stretch modulus are nearly as three to two. These two materials also possess other like characteristics; they are both very brittle, and possess well-developed crystalline structure, so that we may expect the properties of cast-iron under stress to be very faithfully followed by plate-glass.

Material	E .	σ .
Steel	30,000,000	0.25
Wrought iron	28,000,000	0.28
Cast-iron	15,000,000	0.25
Plate-glass	10,500,000	0.23
Nitro-cellulose	260,000 to 300,000	0.40

The high values of the stretch modulus for steel and wrought iron are not, apparently, approached by any transparent material having similar ductile properties, but although nitro-cellulose has a stretch modulus of rather less than one-hundredth that of steel, its stress-strain properties are not unlike. In some recent experiments with a miniature testing machine fitted with an arrangement for recording the stress-strain relations of xylonite throughout the whole range of stress up to fracture, the main characteristics of steel appear on a very much reduced scale, and give additional confidence that the results of optical experiments on this material are applicable to metal structures.

The complete analysis of stress distribution in a plate is not, however, a simple matter, and the analysis of Clerk-Maxwell was intended to provide a solution based on the properties of the isochromatic and isoclinic lines, coupled with the law that the optical effect is proportional to the difference of the principal stresses at a point, and to the thickness of the plate.

A principal stress perpendicular to the bounding planes is assumed to have no optical effect; but since many cases have arisen where there are three principal stress components, it seemed desirable to examine such a case experimentally.

It is a matter of some difficulty to arrange apparatus to stress a specimen in the direction of the incident beam, and at the same time observe the optical effect free from disturbing causes, since a transparent medium must be interposed for applying the required load, and this will be subject to stresses which may interfere with the optical effect on the specimen.

Some observations on circular plates clamped at the edges and uniformly loaded over one face, showed that the bending stresses produced in the plate caused very little optical effect, since the tension and compression stresses neutralise one another, while the shear effects also appeared to be practically negligible. The only remaining stresses of importance were those caused by the clamping plates at the boundary, which produced radial and circumferential stresses having circular symmetry, and as the optical effects of these latter disappeared at a small distance from the edge, a field of view was obtained in which the optical effects of load applied perpendicularly to the

plate were quite small, even when the internal stresses were very great.

Two circular plates clamped together to enclose a space between them may therefore be used as windows for observing the effect of a uniform pressure upon a transparent specimen, which latter may be a plate with its faces parallel to the end plates closing the chamber. If cubical compression is applied by a fluid, the principal stresses in the plane of the plate produce opposing optical effects, and any remaining effect is due to perpendicular pressures on the faces. The arrangement of experimental apparatus therefore took the form of a pair of transparent windows separated by an annular disc, and firmly clamped together by collars. The central chamber so formed was subjected to pressure of air, or other fluid, up to about one thousand pounds per square inch, and afterwards the specimen was introduced and the same pressure applied; but no visible change of effect could be observed. Finally the specimen was set in the field of view outside the chamber, and pressure again applied by the fluid, but still no change was apparent. In all three cases the optical effects produced were small, and practically alike, so that the experimental evidence appears to warrant the conclusion that a principal stress in the direction of an incident beam of polarised light has no optical effect in a thin plate, or at any rate is so small that it may be neglected.

That the retardation between the ordinary and extraordinary rays is proportional to the stress difference perpendicular to the incident beam within the elastic limit of the material may, therefore, be taken as reasonably accurate, although future research may show that it is only an approximation, or even that it is more accurate to commence from a fundamental strain equation; but according to present knowledge there appears to be no warrant for such a procedure.

A more pressing difficulty arises with regard to the optical constant connecting the wave-length retardation with the stress difference. The recent researches of Filon on glass show that the value of this constant is curiously dependent on the previous history of the material, especially as regards its heat treatment. Until further knowledge is gained on this matter it appears to be necessary to guard against errors in stress measurement from this cause by a careful selection and treatment of the material used, since for other artificial bodies we may find that the variation in the constant is not less in magnitude, and is at least as complex as in glass. In some instances the stress optical coefficient may be dispensed with, and Filon has shown, in cases where a theory of stress distribution has been worked out and it is desired to compare it with the results of optical measurements, that the isoclinic lines offer many advantages, since they are independent of photo-elastic constants, and the material need only be subjected to small stresses.

The experimental analysis of stress distribution in a body depends on the possibility of finding the magnitudes and directions of the principal stresses at every point, and in practice it is found the simplest plan to determine the directions of stress from the lines of equal inclination obtained in plane polarised light, and to measure the stress difference by comparison with a wave-length standard, such as a Babinet compensator, or by comparison with a simple tension member set along one of the lines of principal stress, and loaded until the total effect produced is a dark field denoting a zero value. The difference of the principal stresses is then measured in terms of a simple tension. This alone is insufficient to determine the distribution, unless one of the principal stresses is zero, and, in general, another independent measure must be obtained. This is very conveniently supplied by the change in the lateral dimensions of the plate under stress, since this change may be taken, in the absence of a third principal stress, as proportional to the generalised sum of the principal stresses throughout the thickness.

The determination of the lateral strains in a comparatively thin plate, forming part of a model of a machine

or structure, necessitates measurements of extremely minute linear quantities. If, for example, a plate of xylonite is taken, of the maximum thickness obtainable for optical work, a simple calculation shows that these strains must be measured to an accuracy of one or two millionths of an inch. Several instruments have been designed and constructed for this purpose, to fulfil conditions which appear to be essential for successful use. It is necessary to avoid all chance of injury to the surface of a transparent material, so that the measuring points of an instrument can only be pressed lightly against the surfaces, and the weight must, therefore, be supported independently of the model. In instruments so far constructed, the measuring mechanism is carried on a U-shaped frame, for convenience of movement from point to point of the specimen. One measuring needle is secured and operated by a calibrating screw, and the other is free to move a multiplying lever system, and thereby tilt a mirror to give an angular deflection, which latter is calibrated by reference to the standard screw when the instrument has been finally secured in place. In recent work the labour of accurately setting the instrument in a number of different positions has proved so great, that my assistant, Mr. F. H. Withercombe, has designed a useful adjunct in the form of a mechanical slide-rest, to effect the required changes easily and expeditiously. In one arrangement a bracket carries the measuring instrument on a three-point support, and movement is effected by slides arranged to give displacements along three axes at right angles, and their amounts are measured by micrometer screws to an accuracy of rather less than one-thousandth of an inch.

These methods of stress determination avoid the difficulties of the Clerk-Maxwell analysis, which necessitates the determination of the equations to both families of isochromatic and isoclinic bands, usually a mathematical problem of considerable complexity. In some simple cases Mr. Scoble and I have verified the accuracy of the method of lateral measurements for determining the sum of the principal stresses, by comparing the calculated stresses with the experimental values obtained in a plate of transparent material. We have lately carried these experiments a stage further, and have shown that the measured sums of the principal stresses in steel agree with the calculated values. This experimental solution, in fact, gives the stress at a point in a plate, if the conditions are those assumed by the mathematical case of a plate where generalised equations of stress apply.

It is at once obvious, if the utility of experiments on models of this kind is admitted, that experimental evidence is available on a variety of practical engineering problems covering a very wide field of practice, not merely qualitative, but quantitative, and approximating to the needs of the physicist and mathematician, and well within the known variations of the materials with which the engineer has to deal in his daily practice.

During the last few years much attention has been paid to the determination of the stresses in structural elements of primary importance, but only a small number of cases have been examined, since even the simplest problems have proved somewhat difficult and much time and labour have been spent in perfecting optical and mechanical appliances to suit the special conditions required for investigations on transparent models. A simple example of a case easily examined and of practical importance is that of a tension member subjected to an eccentric load. The optical effects here show a linear distribution of stress due to the combination of direct pull and bending, while the neutral axis moves towards the tension side as the stress increases. Not only can these effects be measured, but if the specimen begins to fail some indication is obtained of the way in which the stress distribution is changed to meet the new conditions, and there is found a tendency to an equalisation of the maximum stress at the boundary, although at present the form of the curve of distribution beyond the elastic limit is largely conjectural.

A case like that of a very short member subjected to

direct compression is also not without interest, partly because it reveals unexpected difficulties. In the first place it is not easy to apply a pure compression stress, and if the surfaces in contact are not of the same materials it appears to be practically impossible, since the lateral changes are unlike, and shear stress is therefore produced at the plane of the surfaces in contact. In a short member this shear has a very important influence, and by interposing a thin layer of a material, such as india-rubber, between the pressure plates and the short transparent block, the artificial shear effect produced by the india-rubber is easily shown to influence the distribution throughout, and to increase the stress in a very marked way. Experiments on transparent materials show that the increase of stress may be 20 per cent or even more. Such an effect is known to take place when cubes of stone are crushed between lead plates, and optical investigations on models have enabled a quantitative measure of the effect to be ascertained in this and other cases, thereby confirming the theoretical investigations of Filon on the distribution of stress in such members under various practical systems of loading.

The local effects produced near the points of application of a load are usually of considerable importance, and their influence on the stress distribution in beams has been examined by Carus-Wilson.

The stress effects produced by discontinuities in materials is also of considerable interest, and the cases arising from the necessities of construction are infinite in their variety.

The practical importance of an accurate knowledge of the change in stress distribution produced by changes of section in a member is so thoroughly appreciated that it needs no insistence, and it has received much attention from a mathematical point of view. Thus the local effect of a spherical cavity in a member subjected to uniform tension or compression load has been shown by Love to double the intensity very nearly, while Kirsch has shown that a small cylindrical hole in a tension member trebles the stress intensity. If the hole is elliptical the increase of stress may be still greater, and Inglis has shown, among other interesting cases, that if the minor axis of the ellipse is parallel to the direction of the applied load in a tension member, the stress intensity is increased by an amount measured by twice the ratio of the axis of the ellipse.

A crack, considered as the limiting case of an elliptical hole, is thus seen to give extremely great stresses at the ends, tending towards infinite values for an extremely fine crack.

Optical experiments afford an independent means of examining the alterations of stress intensity produced by discontinuities, and the results are found to agree remarkably well with those obtained from the theory of elasticity. The stress at the boundary of a small cylindrical hole in a plate has been found to be almost exactly three times the stress in the full plate, and the effects of holes comparable with the width of the tension member have also been examined in some detail.

In the case of a rivet just filling the hole and exerting no tangential effect at the boundary, there is a lessened tension stress across the minimum section at the boundary hole, accompanied by a marked radial tension. These effects have been recently confirmed in a mathematical discussion by Suyehiro. Other cases give satisfactory agreement with calculation, and we may therefore feel some confidence that experimental investigation will prove useful in some of the very complicated cases arising out of engineering practice where analysis is difficult if not impossible.

The effects of overstress in materials may also be examined by optical means, and although the laws relating to stress distribution in overstressed transparent material are not known, the general effects observed in simple cases are fairly evident. If, for example, a tension member of glass is stressed, there is no ductile yielding of the material, and the stress will therefore rise very rapidly at the boundary of a small hole, and fracture will therefore occur with

a moderate load. If, however, a ductile transparent material is employed, and the material shows signs of failure at the hole, the breakdown of the structure spreads outwards as the load is increased, until we may have a condition in which within the elastic limit the curve of stress intensity at the minimum section accords with calculation, but at the overstressed part the stress tends to equalise, and the curve of intensity tends to become horizontal near the hole. The mean value of this part of the stress distribution may be inferred from the difference between the total load and the measured values below the region of failure; but the true distribution of the overstress has not been accurately determined, so that the shape of this peak is largely conjectural.

The effects of groups of rivets such as occur in bridges, boilers, and structural members of all kinds, afford ample scope for further inquiry; but before more exact knowledge can be gained of the condition of stress in a complicated riveted joint it appears necessary to examine thoroughly the very simple cases.

Mr. Scoble and I have examined the case of the load applied by one rivet to a plate with various amounts of overlap, and the stresses around the rivet holes have been measured with fair accuracy.

Other interesting cases of discontinuity in structure are afforded by the engine hatchways, gun-turrets, funnel openings, and the like, in ships' decks, and some progress in this direction has been made by experiments on model decks, subjected to loads like those produced when a vessel meets the waves due to a head sea.

Even if the utility of transparent models is left out of account, it is generally acknowledged that many engineering problems are often simplified by the use of models of machines and structures on a small scale, where circumstances forbid experimental examination of the actual work. No defence of their use is, I think, necessary, since the employment of models is a characteristic feature of British methods, not limited to engineers. Kelvin did not disdain their use, and his successors, who have done so much to advance knowledge of the ether and the atomic dust, have freely employed their great ingenuity in the construction of mechanical models and diagrams to explain their views, as in the Lodge cog-wheel diagrams of the ether, the planetary systems of atoms of J. J. Thomson and Rutherford, and the grouping of elements by Soddy.

Engineers have not the same great difficulties which confront those who are advancing the boundaries of pure science; their models are very much what they please to make them; but, even then, problems arise which are sufficiently difficult to tax all the resources of applied science. The behaviour of models considered as similar structures is, therefore, a subject which engineers are bound to investigate in order to determine the effects of fixed and moving loads, the action of wind, the pressure and frictional effects of steam and other fluids, and many other problems.

In the majority of cases the simplest and the most direct method is the experimental study of a model, from which to obtain the data required for calculating effects on a full-sized structure, and hence the laws of similarity have received a very close scrutiny.

Although most valuable information can be obtained from models, their usefulness is clearly limited. The effects of the dead weight of a structure are proportional to the cube of the linear dimensions, and are, therefore, not usually measurable on a model except in exceptional circumstances, as, for instance, where elastic jellies are employed, as in the well-known investigations of Pearson on the stress distribution in reservoir dams. Nor are questions of stability easy to solve, since the forces producing instability are proportional to the size of the model. On the other hand, stress effects due to applications of load may be measured by the strains produced in a model of the same material, if the loads are proportional to the squares of the linear dimensions. The effects of applied load are studied even better in a model constructed of

transparent material, since the variation of stress from point to point can be studied with much greater ease and certainty.

As detailed models of this latter kind present some variations from the usual laws of similarity, it may be of interest to indicate their nature. Questions of deformation clearly involve the elastic constants of the transparent material and their relation to those of the proposed structure, while stress distribution in the solid is influenced by the value of Poisson's ratio. This latter effect is quite small for glass, but may become appreciable with other substance. It is negligible in a model of any material which approximates to a thin plate stressed by forces in its own plane.

The optical effects of any given load are, moreover, independent of the thickness of the material, and depend upon the stress difference, so that colour effects are obtained which may be regarded as pictures of shear stress throughout the model. Modern researches on ductile materials like structural steel indicate that such materials fail at some limiting value of shearing stress, and since the places where these limiting values are reached in the model are visible to the eye, the weak places in the design of a structure can be ascertained and a faulty design corrected by purely experimental means.

In this connection it is of interest to mention that M. Mesnager, the chief engineer of bridges and roads to the French Government, has recently constructed an elaborate model in glass of a design for an arched bridge of about 310 feet span. This investigation was considered advisable for a work of this magnitude constructed of reinforced concrete, in order to check the calculations, especially of maximum stresses in the arched ribs, which latter were assumed to be fixed at the ends.

The effects of reinforcements were allowed for by determining equivalent sections of glass for the members of the model. Many difficulties had to be overcome in the production of a model free from optical defects, but these were all successfully surmounted. The stresses in the model were determined by aid of a Babinet compensator, and formed a valuable check upon the calculations for a structure of this great magnitude and somewhat unusual design.

In this brief and incomplete account of a small branch of applied science relating to engineering the fundamental importance of discoveries in pure science is manifest.

The discoveries in pure science and their innumerable applications to practical ends are ever a potent factor working for the common good, and the value which the British Association places upon applied science was most cordially voiced by Professor Bateson in his Portsmouth Address when he said:—"To the creation of applicable science the very highest gifts and training are well devoted," and, "The man who devotes his life to applied science should be made to feel that he is in the main stream of scientific progress. If he is not, both his work and science at large will suffer. The opportunities of discovery are so few that we cannot afford to miss any, and it is to the man of trained mind, who is in contact with the phenomenon of a great applied science, that such opportunities are most often given"; and, again, "If we are to progress fast there must be no separation between pure and applied science. The practical man with his wide knowledge of specific natural facts, and the scientific student ever seeking to find the hard general truths which the diversity of Nature hides—truths out of which any lasting structure of progress must be built—have everything to gain from free interchange of experience and ideas."

Engineers who are more immediately concerned with the problems of directing the great sources of power in Nature for the use and convenience of man are indeed grateful to our President for these inspiring words, and trust that the ties which unite investigators in pure and applied science will never slacken, but will knit together more closely for a joint advance to a more perfect understanding and utilisation of the laws of Nature.

THE EXTRACTION OF RADIUM FROM
AUSTRALIAN ORES.*

By S. RADCLIFF.

1. A short account was given of all known occurrences of radio-active minerals in Australia.

2. The methods now in use at the Sydney works of the Radium Hill Co. for the extraction of radium from the complex ore found at Olary, near Broken Hill, were described.

3. The results of an examination of the various radio-active precipitates separated in the course of the works operations were given, together with the methods employed in working up preparations of ionium and actinium.

THE CORRELATION BETWEEN THE
SPECIFIC CHARACTERS OF THE TASMANIAN
AND AUSTRALIAN EUCALYPTS.*

By R. T. BAKER, F.L.S., and H. G. SMITH, F.C.S.

IN this paper the authors bring under review the results of their recent research on Tasmanian Eucalypts, comparing them with their own earlier work on the Eucalypts of the mainland, supplemented by more recent data. The ground covered by these investigations, now extending over a period of a quarter of a century, embraces almost the whole geographical range of the genus—an area of the earth's surface of about 3,000,000 square miles. Such an area includes a diversity of soils, climates, altitudes, &c., and naturally one looks for and finds a great variety of species, but it is found at the same time that a relative constancy of specific botanical features and chemical constituents characterises the whole genus.

Comparisons, as well as contrasts, are made of the morphological and chemical features of the trees found at the sea-level and right up to the highest altitudes at which the correlated species occur both in Australia and Tasmania.

Most interesting results have been the outcome of this work, and a theory is now advanced of the geological age of the Tasmanian trees in comparison with those of the mainland. It is also attempted to show that in the Tasmanian Eucalypts we have the more recently evolved of the whole genus.

THE INVERSION OF CANE-SUGAR BY ACIDS
IN WATER-ALCOHOL SOLUTIONS.*

By GEORGE J. BURROWS, B.Sc.

THE rates of inversion of cane-sugar by hydrochloric acid and sulphuric acid have been determined in water-alcohol solutions up to 75 per cent alcohol. In both cases a minimum velocity has been found for a solution containing about 50 per cent alcohol by volume. From the results obtained it is evident that the velocity of inversion is not proportional to the concentration of hydrogen ions in such a series of solvents. The similarity between the curve representing the variation of the inversion velocity with the composition of the solvent and the viscosity curve for these mixtures led the author to conclude that the rate of catalysis by acids is a function of the fluidity of the medium.

The results for the inversion velocity show that the latter is not directly proportional to the fluidity of the solvent. It was assumed that the effect of fluidity on catalysis is similar to its effect on ionic mobility as deter-

mined by electrical conductivity. Hence by dividing the inversion velocity by the conductivity of the acid in the particular solvent the result obtained expresses the activity of the catalytic ion in this medium. In this way it was found that the activity was far greater in 70 per cent alcohol than in water.

It was therefore concluded that catalytic hydrolysis is retarded by the addition of water in the same way as esterification and other similar catalytic reactions.

THE CYANOGENETIC PLANTS OF
NEW SOUTH WALES.*

By JAMES M. PETRIE, D.Sc.

OF the plants growing in New South Wales, over a thousand species have been examined for hydrocyanic acid and cyanogenetic glucosides. Sixty of these gave positive results with sodium picrate paper. These include forty-four species native to New South Wales in seventeen Natural Orders.

Some plants, well known to be cyanophoric in Europe, when grown in this State have never given any reaction, although tested in all seasons.

Only a few were found to evolve free hydrocyanic acid, naturally, but all showed the presence of a glucoside and enzyme.

When the natural enzymes in these plants were killed by boiling water, the reaction to sodium picrate paper ceased; if then a few drops of emulsin, prepared from sweet almonds, were added, positive reactions were again obtained, showing that in all cases the glucosides present in the plants were capable of being hydrolysed by emulsin.

Of the sixty species stated, twenty are grasses, and these include eleven species indigenous to this State. The *Sorghum vulgare* examined by Dunstan and Henry was found to lose its glucoside when fourteen inches high, while the Australian-grown plant retains it when four feet high and mature. Both glucoside and enzyme slowly disappear with air-drying.

One hundred and fifty species of grasses were tested systematically for seasonal variations, and some were found to give negative results at particular seasons. Two species of grasses alone evolved free hydrocyanic acid, and only one of these is available for grazing. This is the only one, except the sorghums, which has been associated with fatalities among stock.

Among the non-cyanogenetic grasses, thirty-three species contain emulsin-like enzymes.

A NEW METHOD FOR DETERMINING THE
SPECIFIC HEATS OF LIQUIDS.*

By ERNST JOHANNES HARTUNG, B.Sc.

THE method described, which was suggested by Professor Orme Masson, is a modification of the mixture method for determining specific heats. The principle consists in measuring the lowering in temperature of a known amount of the particular liquid on the introduction of a definite weight of dry ice contained in a thin glass bulb. The calorimeter is a thin glass vessel of about 100 cubic centimetres capacity, and is supported inside a silvered Dewar tube. A well-fitting rubber stopper closes the mouth of this tube, making the apparatus air-tight. Through the stopper is fitted a Beckmann thermometer, and also a thin glass stirring rod, the lower end of which is suitably shaped to receive the small ice-bulb. A third hole, lined with glass and closed with a well-fitting glass stopper, passes through the rubber stopper and serves for

* Read before the British Association (Section B), Australia Meeting, 1914.

* Read before the British Association (Section B), Australia Meeting, 1914.

the introduction of the ice-bulb. This last consists of a small sealed thin glass cylindrical bulb, containing a definite weight of distilled water and also as much silver gauze as possible. The last ensures rapid heat conduction, and makes the bulb heavy enough to sink in dense liquids. The bulb is suspended by a fine platinum wire.

The liquid to be experimented with is introduced into the calorimeter by means of a standardisation pipette, and the apparatus is closed until constant temperature is attained. The ice-bulb has meanwhile been frozen in a mercury bath supported in an ordinary freezing-point apparatus. When the temperature of the mercury is constant at from -3° to -4° , the bulb is removed by its suspension and rapidly introduced into the lower part of the stirring-rod in the calorimeter. The liquid is then stirred by hand until constant temperature is again attained, which usually requires about three minutes. Radiation corrections are then applied, and the specific heat of the liquid calculated, the heat capacity of the ice-bulb being accurately known. The experiments should be performed in a room regulated to constant temperature.

The advantages claimed for the method are its simplicity, its rapidity, and its accuracy. Experiments with water at 25° C. gave consistent results agreeing to within 0.4 per cent. When ether was used, it was found necessary to coat the rubber stopper with tin-foil in order to protect it. The results with ether at 25° C. agreed to within 1.4 per cent (the vapour-pressure of ether at this temperature is 545 mm.). The specific heats of several sulphuric-acid-water mixtures were also measured and compared with the classical results of J. Thomsen. The average divergence was less than 1 per cent. Further measurements with different liquids are now in progress.

The apparatus described is not suitable for a viscous liquid (such as glycerin) owing to inefficient stirring. By having another liquid than water in the carrier-bulb, the scope of the method can probably be extended.

THE INFLUENCE OF WEATHER CONDITIONS UPON THE AMOUNTS OF NITRIC ACID AND OF NITROUS ACID IN THE RAINFALL NEAR MELBOURNE, AUSTRALIA.*

By V. G. ANDERSON.

DAILY determinations of the amounts of nitric acid and of nitrous acid in the rainfall at Canterbury, near Melbourne, have been made since November 1, 1912. The results to February 28, 1914, when correlated with meteorological data for Melbourne and daily isobaric charts of Australia, reveal the existence of a relation between weather conditions and the amounts of nitrogen acids in rain-water.

The concentration of nitric acid reached a maximum in summer, a minimum in winter, and an intermediate position during autumn and spring. The concentration of nitrous acid reached a maximum in winter and a minimum in summer. The ratio of nitric nitrogen to nitrous nitrogen was highest in summer and lowest in winter. On many occasions during winter the ratio was approximately as 1:1. A relation between atmospheric temperature and this ratio was noted. Its nature was shown by plotting the mean minimum temperature of each month with the mean monthly ratios, the curve being of the same type as those which express changes of chemical velocity with temperature. The ratio is doubled for equal increments of temperature. From the results it would appear that in rain-water nitric and nitrous acids are formed in equal molecular proportions, and that, if the ratio could be determined instantly, or before any change could ensue, it would invariably be as 1:1. In cold weather the velocity is retarded to such an extent that

little change occurs even after comparatively long periods; hence the increased amounts of nitrous acid found in winter. In hot weather, the velocity being greatly increased, the residual amounts of nitrous acid are very small, nearly all having been converted into nitric acid. The facts point to atmospheric nitrogen peroxide as the source of nitric and nitrous acids in rain-water, as this gas reacts with water, forming these acids in equal molecular proportions.

In a graph plotted with daily concentrations of total (nitric plus nitrous) nitrogen as abscissæ, and with rainfall as ordinates, the points are found to arrange themselves into a series of rectangular hyperbolæ. Further, each group of points lying along a particular curve is found to correspond with falls of rain occurring during one particular type of weather. From this it follows that for a particular type of weather (1) the concentration of oxidised nitrogen varies inversely as the rainfall; (2) the product of the concentration and the rainfall is constant; (3) the total weight per unit area of oxidised nitrogen precipitated with rain falling during twenty-four hours is constant. In brief, the amount of oxidised nitrogen per acre carried down by rain falling on any day is a function of the type of weather, and, within certain limits, is independent of the amount of rainfall. These facts may be explained by assuming that for each type of weather there exists in the air a definite concentration of nitrogen peroxide, and that this soluble gas is completely washed out of the air by the first portions of a shower; any further rain falling through the now purified air not increasing the amount of oxidised nitrogen in the rain-water, but, by dilution, decreasing the concentration.

Nine well-defined recurring types of weather have been investigated. These may be classified into three groups as follows:—(1) Antarctic types; (2) tropical types; (3) divided control (Antarctic and tropical) types. The accompanying table shows the number of examples of each type investigated, together with the oxidised nitrogen constant in pounds per thousand acres, for each type.

	Number examined.	Oxidised nitrogen constant, pounds per 1000 acres.
Antarctic types—		
A-shaped Antarctic depressions	(a) 35	1.5
	(b) 28	2.5
	(c) 10	4.1
Tropical types—		
Tropical (or monsoonal) depressions	(g) summer and autumn type ..	6
	(h) summer type ..	3
	(i) "heat-wave" type ..	2
Divided control types—		
(d) Antarctic depressions with slight tropical influence ..	6	6.1
(e) Antarctic depressions with strong tropical influence ..	4	8.5
(f) Tropical depressions with slight Antarctic influence ..	5	12.0

A NEW METHOD FOR THE DETERMINATION OF VAPOUR-PRESSURES AND AN EXAMINATION OF A SOURCE OF ERROR IN CERTAIN DYNAMICAL METHODS.*

By F. H. CAMPELL, M.Sc.

SINCE none of the accepted methods is suitable for the determination of the vapour-pressure of a binary mixture of a volatile with a non-volatile liquid a new method has been devised for the purpose.

The principle used is that of allowing a liquid saturated with a suitable gas, usually hydrogen, to evaporate into an

* Read before the British Association (Section B), Australia Meeting, 1914.

* Read before the British Association (Section B), Australia Meeting, 1914.

enclosed space filled with the same gas at the same temperature and pressure, the latter being approximately atmospheric. The extra pressure exerted by the vapour is measured by means of an open mercury manometer after the volume has been restored to its original value by means of a levelling vessel. The method can be applied to volatile organic liquids of many kinds, since they come into contact with glass and mercury only. The liquid is enclosed in a glass tube projecting through a rubber stopper, which closes an opening at the bottom of the vessel, the stopper being protected from the action of the liquid by a layer of mercury. When the apparatus has reached the temperature of the constant temperature bath in which it is immersed, the tube, previously deeply scratched, is broken by gentle sideways pressure on the projecting end. Saturation of the gas by the vapour is hastened by gently shaking the apparatus.

Experiments have been made with the following liquids and gases:—Methyl alcohol, ethyl alcohol, diethyl ether, carbon disulphide, chloroform, and water, evaporating into carbon dioxide, air, hydrogen, and, in the case of chloroform, nitrogen in addition. In every case the values obtained, though very concordant, are lower than the most reliable results obtained by the ordinary static method. The magnitude of the error evidently depends on the solubility of the particular gas in the particular liquid as it diminishes in each case, except that of water, in the order carbon dioxide, air, hydrogen. With water at 60° C. the results obtained with air and hydrogen are practically identical. The error when hydrogen is used is generally less than 1 per cent, and it is considered that the agreement is sufficient, as with mixtures the ratio between the observed pressure of the solution and that of the pure volatile solvent is to be considered. With air the errors are from 2 to 6 per cent, and it is concluded that methods depending on the saturation of a current of a gas passing through or over solution and pure solvent must therefore involve more or less error from this cause, a fact which does not seem to have been appreciated in the past. Perman (*Proc. Roy. Soc.*, 1903, lxxii., 72) and Krauskopf (*Journ. Phys. Chem.*, 1910, xiv., 489) obtained satisfactory results with water, although those of Regnault (*Ann. Chim. Phys.*, 1845, [3], xv., 129) and Tammann (*Wied. Ann.* 1888, xxiii., 322), which are lower than those obtained by the static method, are brought into satisfactory agreement with these upon the author's assumption, which indicates that the errors introduced by the presence of a dissolved gas are negligible under certain conditions.

THE ATOMIC WEIGHT OF LEAD FROM PITCHBLLENDE.

By O. HÖNIGSCHMID and Mlle. St.-HOROVITZ.

RECENT theories show that the final disintegration product in the uranium-radium series, known as radium G, should be an element isotropic with lead, that is to say, inseparable from it by chemical methods, although possessing a different atomic weight.

Radium is formed from uranium by the liberation of three α -particles, and radium G from radium by the liberation of five particles. According to the determinations of one of us $U - Ra = 238.18 - 225.97 = 12.21$ (O. Hönigschmid, *Monatsh. f. Chemie*, 1913, xxxiv., 213; *Wiener Akademischer Anzeiger*, No. III., January 22, 1914). This gives a decrease of 4.07 for the emission of one α -particle. Then the atomic weight of radium G ought to be $225.97 - 5 \times 4.07 = 205.62$.

As the purest pitchblende, with 60 per cent of U_3O_8 , also contains 2 or 3 per cent of lead, it is possible that part at least of this lead is radium G; the atomic weight of lead extracted from pitchblende ought to be lower than that of ordinary lead by an amount corresponding to the quantity of radium G it contains.

The Academy of Sciences at Vienna placed at our disposal some lead chloride obtained from the residues of the treatment of pitchblende for the preparation of radium salts. This chloride was first dissolved by ammonium acetate and then precipitated as sulphate. The sulphate was washed, re-dissolved in ammonium acetate, and transformed into sulphide which was then converted into nitrate. The nitrate was submitted to crystallisations by solution in warm water and precipitation with concentrated nitric acid, the little crystals being drained each time by centrifugation in a platinum apparatus. The purified nitrate was again transformed into chloride, and the latter was subjected to solutions in a saturated solution of hydrochloric acid gas, carried out in silica vessels, followed by precipitation with water. Finally the chloride was fractionated by fresh crystallisations in pure water. The product obtained satisfied all the conditions of purity required in a chloride of lead intended for an atomic weight determination.

The analysis of this chloride was carried out by the two methods employed by Baxter for the determination of the atomic weight now adopted for lead, one method being solely gravimetric, while the other is founded on the use of the nephelometer.

The results obtained were as follows:—In a series of six experiments in which the weight of $PbCl_2$ varied from 1.97691 grms. to 3.33164 grms., the determination of the ratio $PbCl_2$ to $2AgCl$ gave for the atomic weight of lead numbers ranging from 206.719 to 206.749, the mean being 206.732. Another series of three experiments, in which the weight of $PbCl_2$ ranged from 3.22459 grms. to 3.49447 grms., gave, for the direct determination of $PbCl_2$ to $2AgCl$, atomic weights varying from 206.730 to 206.748, the mean being 206.741.

The mean of these two means gives for the atomic weight of lead obtained from pitchblende the number 206.736, lower by 0.4 than the atomic weight of ordinary lead.

It is possible that one can extract from a pitchblende (free from isolated fragments of blende) a lead of still lower atomic weight. Researches in this direction are in progress.

The determinations which are the subject of this note were communicated to the Congress of the Bunsen Gesellschaft at Leipzig, May 23, 1914, and to the German Chemical Society at Berlin. They confirm the theory of the existence of elements possessing identical chemical properties but different atomic weights.

Similar results have recently been communicated to the Academy by M. Curie (*Comptes Rendus*, 1914, clviii., 1676; *CHEM. NEWS*, cx., 94). They are in agreement with the above.—*Comptes Rendus*, 1914, clviii., 1796.

ATOMIC WEIGHT OF LEAD OF RADIO-ACTIVE ORIGIN.

By TH. W. RICHARDS and M. E. LEMBERT.

MAURICE CURIE (*Comptes Rendus*, 1914, clviii., 1676; *CHEMICAL NEWS*, cx., 94) and O. Hönigschmid and Mlle. St. Horovitz (*Comptes Rendus*, 1914, clviii., 1796) having published their researches on this subject in the *Comptes Rendus*, we take this opportunity of giving the result of our experiments, as they were undertaken independently of those of the above named authors and first led to a definite result. (Communicated by K. Fajans to the Chemical Society of Karlsruhe, May 8, and to the Congress of the Bunsen Gesellschaft at Leipzig, May 23; our detailed publication, *Journ. Amer. Chem. Soc.*, 1914, xxxvi., 1329).

After nine months of work, undertaken at the suggestion of M. Fajans in the Chemical Laboratory of the University of Harvard, we have obtained a direct proof of the

theory established by Fajans and Soddy, viz., that certain elements have different atomic weights while exhibiting identical chemical as well as spectroscopical properties. Basing our work on the conclusions of the above authors, we chose lead as the element for investigation.

Let us call to mind briefly two points:—Firstly, the atomic weight of lead obtained from the successive decomposition of uranium and radium ought to be 206.0, given that the atomic weight of radium is 226.0 and that each α -ray decomposition results in a loss of mass of 4 units. Secondly, that the atomic weight of the non-radio-active member of the lead group coming from thorium ought to be 208.4, while that of ordinary lead is known to be 207.1.

Our analytical processes were practically those adopted by Baxter and Wilson in their work on the atomic weight of lead. After having submitted lead chloride obtained from different minerals to many purification processes we crystallised it several times in silica and platinum vessels.

It was not difficult to obtain in each case a chloride of lead which was so pure that no chemical or spectroscopical method could reveal in it the presence of the least impurity of any importance.

The perfect purity of the specimens of lead which we analysed was proved by the fact that when we continued the process of purification we found the same value for the atomic weight.

Method of Analysis.—The lead chloride, dried in the desiccator, was heated to fusion in a current of hydrochloric acid gas and nitrogen. After cooling it was weighed and then dissolved in a large quantity of water. Finally the chlorine was precipitated with silver nitrate. By this method in absolutely identical conditions we performed parallel analyses of ordinary lead and lead extracted from radio-active minerals.

Although we were less interested in establishing absolute than relative values we may call attention to the agreement of our number (given below) for ordinary lead and the corresponding number in the International Table, seeing that this agreement is an argument in favour of the correctness of our measurements.

The details of the analysis and of the purification processes will be given in our complete article.

The following are the results:—

Lead from carnotite (Colorado)	206.59	± 0.01
" " pitchblende (Joachimsthal) ..	206.57	± 0.02
" " " (N. Carolina) ..	206.40	± 0.05
" " " (Cornwall) ..	206.86	± 0.02
" " " thorianite (Ceylon)	206.82	± 0.01
Ordinary commercial lead	207.14	± 0.01

The spectrum of lead from carnotite is identical with that of ordinary lead.

For the detailed discussion of the results from the theoretical point of view we may refer to the work of Fajans (*Die Naturwissenschaften*, 1914, II., 543; *Sitzber. Heidelberger Akad. d. Wiss.*, 1914, 11). It will be sufficient to mention here that the four first minerals are uranium minerals practically free from thorium, for which we are indebted to Sir William Ramsay and W. B. Boltwood, E. Giesel and K. Fajans. In the pitchblende from N. Carolina we had an extremely pure material, and its atomic weight differs most from that of ordinary lead. The thorianite contained, besides 60 per cent of thorium, 22 per cent of uranium, and thus also lead from uranium.

Soddy, moreover (*Journ. Chem. Soc.*, June, 1914), has performed two analyses of the lead of thorite containing little uranium, and has found as the mean theoretical value 208.4; but this result cannot be regarded as definite. The results of M. Curie and of Hönigschmid and Mlle. Horowitz agree well with the preceding.

In order to determine precisely the quantitative relations it seems to us that it would be useful to obtain some experimental data; we, therefore, intend to continue these researches.—*Comptes Rendus*, clix., 248.

SYNTHETIC RESINS.*

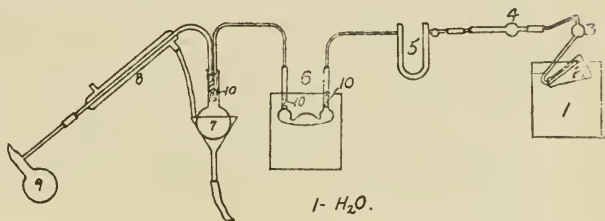
By L. V. REDMAN, A. J. WEITH, and F. P. BROCK.

(Continued from p. 119).

By-products Formed in the Reaction between Anhydrous Phenol and Dry Hexamethylenetetramine. (These experimental results were obtained in our laboratories by Mr. Weston Carpenter).

AN apparatus was arranged as shown in the accompanying diagram. A flask with a long side delivery tube was sealed off after the hexamethylenetetramine and phenol were added. The delivery tube led into a reflux condenser, thence into a safety trap, sulphuric acid Marchand U-tubes, and finally through a CaCl_2 tube and safety bulb into a gas-trap over water.

The flask containing the hexamethylenetetramine and phenol was then heated carefully. Great care was necessary as the reaction is rapid, being strongly exothermic, so that it goes at an increased rate even after the flame is removed if the initial heating has not been sufficiently slow



- 1- H_2O .
- 2- Gas trap.
- 3- Safety bulb.
- 4- CaCl_2 tube to keep experiment dry.
- 5- CaCl_2 tube in exp.
- 6- H_2SO_4 Safety cooled.
- 7- H_2SO_4 trap, cooled.
- 8- Condenser.
- 9- Distilling flask.
- 10- Glass wool.

to allow the first of the reaction to take place at a moderate rate until the ammonia has been partly evolved. Checks were kept upon the reaction in four ways:—

1. The loss in weight in the flask.
2. The increase in weight in the Marchand tubes.
3. Titration of the ammonia which came over by boiling it off from the $(\text{NH}_4)_2\text{SO}_4$ on the addition of KOH.
4. Direct titration of the ammonia in duplicate experiments.

Table II. shows the result of three experiments.

The results show that the loss in the flask agrees very closely with the calculated yield of ammonia from the hexamethylenetetramine used. The titration of the ammonia here, as in many other experiments, has practically always been 100 per cent of the nitrogen present, and the gain in the concentrated sulphuric acid just equals the calculated NH_3 and agrees also with the loss from the flask.

Care was taken to include, in the final weight of the flask, the weight of phenol found in the washings from the reflux condenser and the trap. This generally amounted to less than 0.05 gm. of phenol.

To prevent the escape of any ammonia in the rubber joints the glass tubes were placed end to end, over which was drawn very thick walled rubber tubing which previously had been given a heavy coat of pyroxylin varnish.

In the Marchand U-tubes some care was needed to prevent the sulphuric acid from splashing as the ammonia absorbed rapidly and the sulphuric acid struck back. This was overcome by absorbing part of the ammonia in a small amount of sulphuric acid in the first tube and the remainder of the ammonia in the second tube. Glass-wool

TABLE II.

Expt.	Amount of hexamethylenetetramine, in grms.	Phenol used, in grms.	Calculated yield of NH_3 , in grms.	Loss in flask.	Gain in H_2SO_3 tubes.	Titration of NH_2 .	Per cent error.		
							1.	2.	3.
1.	4.000	41.730	1.943	1.954	1.930	1.937	+0.56	-0.6	-0.3
2.	4.000	40.370	1.943	1.943	1.943	1.950	0.0	0.0	+0.3
3.	4.000	41.510	1.943	1.954	1.930	1.940	+0.56	-0.6	-0.1

plugs prevented the splashing and the results are fairly concordant. Simple as the reaction would seem to be, the very rapid evolution of the ammonia in the early part of the experiment made a number of experiments necessary before the present apparatus was devised and the ammonia could be absorbed in its rapid evolution without allowing any of it to escape.

We concluded then from these experiments that no water is formed in the reaction or it would be evolved during the boiling which takes place at 180°C . for two hours, and the loss in the flask would not equal the calculated loss for ammonia and the actual weight of ammonia found by titration and by weighing as $(\text{NH}_4)_2\text{SO}_4$. It was not considered sufficient to simply weigh the ammonia coming off, as methylamines if present would increase the weight and give useless results. Nor was the titration alone sufficient as it did not distinguish between ammonia and methylamines. The two experiments were necessary in order to check up the results and to make certain that no other product than NH_3 is evolved during this reaction between phenol and hexamethylenetetramine. The resin which formed in the flask was the soluble, fusible phenyl-endeke-saligeno-saligenin dissolved in the excess phenol.

THE ACTIVE HYDROGEN ON THE BENZENE NUCLEUS.

The hydrogen which is replaced in the ring is apparently very largely the ortho hydrogen, although either the meta- or the para-hydrogen may possibly be replaced. This reaction is similar to the formation of orthoxy-benzylalcohol when phenol and formaldehyde are treated in the presence of NaOH .

To test this statement, three experiments were undertaken with the cresols:—5.1 grms. of each of the pure cresols were weighed out separately into test-tubes and to each 1.1 grms. of hexamethylenetetramine were added. The three test-tubes were placed in a thin beaker which rested on a block of wood, in an electric oven at 135°C . In a few minutes the meta-cresol began to react, giving off ammonia and passing over into an insoluble, yellow, scoriaceous resin, which, when hot, was rubbery for a very short time, but soon transformed into a hard non-rubbery resin at 135°C .

The para-cresol acted in the same way as did the meta-cresol although slightly slower. The two resins were identical in appearance and general properties.

The ortho-cresol acted very differently. After three days of heating the reaction had proceeded only far enough that the mass was a viscous, yellow liquid when hot (135°C .) and a brittle solid when cold. The reaction was very slow and did not evolve ammonia rapidly at any time. When heated at 200°C . for thirty minutes it formed into a rubbery, resinous mass when hot and a hard rather brittle solid when cold.

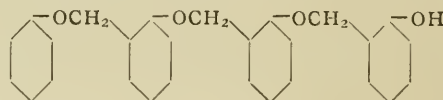
On the whole, then, the para- and meta-cresols acted rapidly and similarly, while the ortho-cresol acted very slowly and did not form a resin which when hot was hard and solid.

This delayed reaction of the ortho-cresol may be explained as a steric hindrance for the hydroxyl.

It may also be explained as due to a substitution of half the active (ortho) hydrogen in the ring by a non-reactive group. The latter seems the more probable. The fact that the meta- and para-cresols are very rapid in reaction seems to indicate that the meta- and para-hydrogens are not the ones which are replaced during the formation of the synthetic resin.

THE ACTIVITY OF THE HYDROGEN IN THE HYDROXYL GROUP.

Of the proposed formula for these condensation products, the more reasonable seems to be the straight chain formula with the phenol rings linked together with the $-\text{CH}_2\text{O}-$ group in between, the attachment being made at the hydroxyl of the phenol and at the ortho hydrogen of the ring as follows:—



The reason for assuming that the reaction is closely connected with the hydroxyl group lies in the fact that if the hydrogen of the hydroxyl or the hydroxyl itself be replaced by a non-reactive group, no apparent reaction takes place after prolonged heating either in the dry or in wet processes. For example, if anisole be heated at the boiling-point with hexamethylenetetramine in the absence of water for one week continuously, no appreciable reaction takes place. The anisole remains a colourless, transparent, mobile liquid with the anisole odour, and the hexamethylenetetramine settles out on cooling as a crystalline salt. The salt was tinged slightly yellow but further than that no reaction was noticeable.

If the hydroxyl be replaced by hydrogen, *e.g.*, if naphthol be replaced by naphthalene, no reaction takes place after prolonged heating in the dry or wet, while with β -naphthol in the absence of water the reaction is very rapid.

THE REPLACEMENT OF THE HYDROXYLS IN THE RESINS BY NON-REACTIVE GROUPS.

The fact that phenol-formalin resins, made up into lacquers and heated in thin films insoluble in alcohol, acetone, &c., are attacked slowly by caustic potash leads one to the conclusion that whatever substance is formed it very probably contains a percentage of free hydroxyl. So long as the hydroxyls are present it is to be expected that the substance remains at least partly or slowly soluble in free caustic.

Working upon the assumption that the reaction continues as an open chain of benzene rings linked together by the group $-\text{O}-\text{CH}_2-$ which does not finally form a closed ring or an inner anhydride, it was desirable to fill the hydroxyl on the end of the long chain with an inert group, or to replace the hydroxyl entirely.

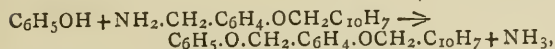
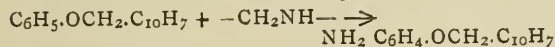
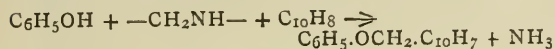
The similarity of anisole and phenetol to phenol and the inertness of their alkylated hydroxyls suggested their use in small quantities in making caustic insoluble resins.

A resin was made up consisting of 6 mols. phenol, 1 mol. anisole, and 1 mol. hexamethylenetetramine. The mixture was heated for a short time in an open beaker and cooled while still liquid. The resin was a light transparent amber-yellow colour, solid at ordinary temperatures and soluble in alcohol and acetone, although more slowly soluble than the ordinary resins made up without the addition of anisole.

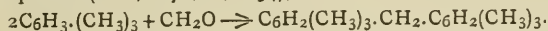
When made into a lacquer and cooked at 170°C . on brass sheets it gave a light transparent film which was insoluble in acids, alcohol, acetone, and N -caustic potash. It required seventy-two hours to loosen the film with the caustic. All lacquer films from resins made of phenol and an active methylene, whether made in the presence or absence of water with or without the ordinary condensing

agents, are attacked by N-caustic within twenty-four hours, the lacquer coating reddening in a short time after the caustic is added. The film from resins compounded of 6 mols. of phenol and 1 mol. of anisol or phenetol remained unreddened and quite unattacked by the N-caustic potash at the end of the first twenty-four hours, and at the end of seventy-two hours was only slightly attacked along the edges of the coated brass strips and at no time was any reddening of the lacquer film noticeable.

The explanation for this increased insolubility of the resin and of its greater resistance to colour changes seems to lie in the absence of free hydroxyl. This is best illustrated for naphthalene from the following equations:—



&c., and this reaction may continue indefinitely. This resin would no longer have the properties of a substance possessing free hydroxyls, but it would display the inert characteristic of an ether-like anisol which is not broken down in the presence of boiling caustic potash. That such a reaction is possible may be inferred from Baeyer's work with mesitylene and formaldehyde, giving, according to the equation (*Ber.*, 1872, v., 1094),—

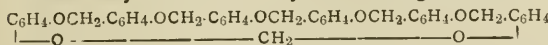


If the hydrogen in a mesitylene ring is active in the presence of CH_2O and forms water with the oxygen of the formaldehyde, leaving a substance formed by dehydration behind, it is not unreasonable to assume that at high temperatures (180°C.) a hydrogen on the naphthalene ring may be sufficiently active to form ammonia with an amine group, and leave a resin as a by-product which has no free hydroxyl at the end of the molecular chain as described above. The permanence in the yellow colour of the resin or lacquer, and their insolubility in normal caustic as well as all other solvents, point to the absence of free hydroxyls in the substance.

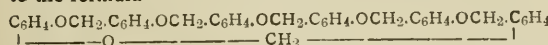
THE FINAL PRODUCT—THE INSOLUBLE INFUSIBLE RESINS.

The transformation of the phenyl-endeka-saligeno-saligenen into the final insoluble infusible resin is brought about by the further condensation of its molecules by active methylenes.

Dr. Baekeland concludes that the final product is not obtained through the polymerisation of novolak as an intermediate product, but that the growth of the chain stops when six phenols have entered, and that an extra hydrated formaldehyde forms with the six phenol chain an inner anhydride as shown by the following formula:—



This inner anhydride, he assumes, polymerises into the insoluble infusible resin. That this cannot be the mechanism of the reaction in the case of the production of these synthetic resins by means of anhydrous hexamethylenetetramine, is evident from the fact that no water or oxygen is present which could possibly form such an inner anhydride as above described. If the reaction takes place with the formation of the larger ring it would be according to the formula—



and would lack at least one oxygen in the molecule which the inner anhydride formula requires. This oxygen might, in certain cases, be replaced by nitrogen although this is improbable, as the final product never yields more than a trace of nitrogen, and even this amount may be mechanically locked as ammonia in the final product.

Further, it may be mentioned that the larger molecule of phenyl-endeke-saligeno-saligenin, *i.e.*, 13 mols. of phenols: 12 mols. of methylenes, could not, without hydrolysing into a shorter chain, yield such a molecule as Dr. Baekeland proposes.

Recently, Dr. Raschig (*Zeit. f. Angew. Chem.*, 1912, xxv., 1945) has proposed certain formulæ for the condensation of phenols and active methylenes which, apparently, are not identical with any of the substances isolated as products of this reaction. His formulæ show that in passing from "Bakelite I" to "II" the carbon content increases from 77 per cent to 81·4 per cent, while in actual results all the combustion analyses of Bakelite which Dr. Baekeland has published and the analyses which we have carried out of these synthetic resins, show that the carbon content decreases from 78·1 per cent to 79 per cent or lower as the resins pass from the soluble to the insoluble state. As these proposed formulæ evidently do not agree with actual analyses they will not be considered further.

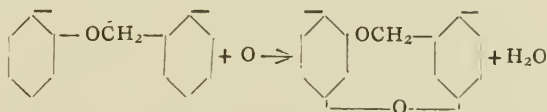
In arriving at an empirical formula for the final resin, a series of combustion analyses were carried out on products prepared as described in the following table:—

Preparation of resin.	C.	H.
The insoluble material from a resin hardened with formaldehyde and washed free of substances soluble in normal NaOH ..	75°58	6°08
	75°34	6°11
A 6:1 resin containing traces of anisol heated in air at 175° C. for six hours, then pressed in a mould at at 12,000 lbs. per sq. in. for five minutes at 200° C.	74°56	6°40
	75°01	4°50
	74°74	6°35
	75°32	6°55
	75°02	6°35
6:1 resins heated at 200° C. for 100 hours	78°83*	5°47
	75°58	5°20

* Unaccountably high.

The average of the eight analyses gives C = 75.4, H = 5.9, O = 18.7, which corresponds to $77(\text{C}_7\text{H}_6\text{O}) \cdot 20(\text{C}_7\text{H}_4\text{O}_2)$.

The group $C_7H_4O_2$ may be explained as an oxidation in which two hydrogens are replaced by an oxygen somewhat as follows:—



Simultaneous with this oxidation is a reddening which takes place rapidly at increased temperatures, *i.e.*, above 200° C. The oxidation probably reaches an equilibrium at $49(\text{C}_7\text{H}_6\text{O}) \cdot 48(\text{C}_7\text{H}_4\text{O}_2)$.

(To be continued).

NOTICES OF BOOKS.

The Making of Leather. By HENRY R. PROCTER, M.Sc., F.I.C. Cambridge: The University Press. 1914.

THIS book contains an interesting discussion of the scientific basis of the leather industry, such as the average well-informed reader will find entertaining and instructive. It is not intended to be used as a manual by leather manufacturers, and practical details are not given very fully. The difficulty of deciding how much previous scientific knowledge the reader may be supposed to have is satisfactorily surmounted by the author, and he gives a very intelligible account of the elements of chemistry in so far as a knowledge of them is required for understanding the preparation of leather. The structure of the skin is de-

scribed in some detail and the various processes through which skins pass before the final product is obtained are outlined. The book is an excellent example of a thoroughly scientific and yet popular exposition, and will undoubtedly be found one of the most interesting of the series of Cambridge manuals to which it belongs.

The Topographic Features of the Desert Basins of the United States with reference to the Possible Occurrence of Potash. By E. E. FREE. *Bulletin of the U.S. Department of Agriculture.* 1914.

THE author of this bulletin was commissioned to make a thorough investigation of the desert basins or undrained areas of the United States, with a view to ascertaining their possible value as sources of potash. For this purpose he collected topographic data from various sources—the sheets of the United States Geological Survey, and other maps, and also by personal travel—and thus obtained information for the preparation of maps giving the boundaries of the various basins. The number of inclosed basins amounts to some 200, but many obviously lack all practical value on account of the smallness of their area or for other reasons. However, the investigation clearly shows that in all probability the United States possesses large stores of potash which are as yet practically untouched.

The Utilisation of Petroleum and Natural Gas in Wyoming. By W. R. CALVERT. Washington: Government Printing Office. 1913.

IN this pamphlet the author describes his investigation of the utilisation of oil and natural gas in Wyoming, the main purpose of which was to discover what waste, if any, accompanies the industry. He found only very few instances of such unnecessary waste, and hence the paper is chiefly an account of conditions, and only very occasionally are suggestions and recommendations made for preventing loss of material. The bulletin also contains a paper by George A. Burrell on the suitability of natural gas for making gasoline, in which the plant usually employed is described, and details of the cost of running, &c., are given. The bulletin is naturally of chief local interest, and is to be regarded as of a preliminary nature only.

Gravitation and Aether Waves. By Colonel F. W. BADOLEY, A.I.C.E., F.R.G.S., F.R.M.S.

THIS pamphlet contains a letter written to *Knowledge* by the author, together with some explanatory notes. He claims to have proved that gravitation is due to the aether transverse wave force acting on molecules and drawing them towards the point of origin of the aether wave. The pamphlet contains little beyond dogmatic assertions, based apparently upon general considerations, but within the limits of a short letter it is clearly impossible to give anything more than the merest outline of a discussion of a subject of such great moment.

On the Isomorphy of the Ethylsulphates of the Metals of the Rare Earths and on the Problem of the Eventual Morphotropic Relations of these Salts with Analogous Salts of Scandium, Indium, and Beryllium. By Prof. F. M. JAEGER. Amsterdam: Koninklijke Akademie van Wetenschappen. 1914.

THE object of the research described in this paper was to find out any relation between the changes of the crystallographical parameters which are caused by the substitution of the trivalent atom Me''' in the molecule Me_2''' ($SO_4.C_2H_5)_6 + 18H_2O$ by any other atom of the rare earth series, and between the changes in molecular weight simultaneously produced by this substitution. The author also hoped that he might get some information about the parallelism between the changes of the atomic weights and those of the atomic or molecular volumes of the rare earths or their analogous compounds. Full tables of the

numerical data obtained are given, and it is pointed out that all the ethyl sulphates of the rare earth metals belong to a perfectly isomorphous series. Possibly more detailed research will show that the atomic volume curve possesses a single or double periodicity in this group.

The Public Utility of Museums. Copy of Official Debate, May, 1914.

IN the Parliamentary debate, of which this is the report, the question of the provision of official guide lecturers in the London museums was thoroughly discussed, and statistics of the number of people who availed themselves of their services were given. The results appear to have been highly satisfactory in nearly all cases, and the return dealing with provincial museums will be awaited with interest.

MISCELLANEOUS.

Tribenzoin.—L. Balbiano.—It has been found that the partial saponification of benzene with sodium alcoholate in presence of absolute alcohol gives glycerin, ethyl benzoate, and unaltered tribenzoin, while the etherification of glycerin by benzyl chloride gives only tribenzoin. The author has further investigated these two reactions in order to ascertain whether they take place in different stages, but has not arrived at definitely conclusive results. —*Atti della Reale Accademia dei Lincei*, xxiii., [1], No. 9.

American Chemical Society.—We regret to inform our readers that the Montreal meeting has been indefinitely postponed, and it now seems improbable that any meeting of the Society will be held this fall for the reading of papers. The following extracts from a letter from Prof. R. F. Ruttan, Chairman of the Committee, explains the final decision:—

We had a meeting of the Executive Committee this afternoon, and decided that the meeting could not be made to go in British territory this autumn.

Canada is sending the first contingent of 20,000 very soon, and a second and third will follow.

Montrealers feel that we are at war with Germany and Austria, and are behaving as if the enemy were threatening us.

The harbour, canals, &c., are under Martial Law. The excursions were off, as the company cancelled our contracts, for the steamers for the rapids and harbour.

No German member of the Society would naturally come to British soil, and all with German names would be questioned at the boundary. Many are even now turned back. We felt that the exclusion of so many prominent members of the Society was a high price to pay for a meeting here.

Any foreigners would be subjected to disagreeable formalities and conditions on coming here just now.

It would be impossible to attract to the Convention the slightest public interest in Montreal, outside a few dozen chemists. No one would come to the Conversazione or the Garden parties we had arranged, and while there would surely be the feeling of good fellowship among ourselves, it would be overshadowed by the tragic war we are in at present.

It is sad to look over the wreck of our hopes of a big and successful meeting.

Everything was organised and under way, even to rehearsing for the smoker. The toastmaster and speakers for the banquet, the chemical and other scientific "stunts" for the Conversazione were arranged, the hall for the exhibits prepared, which, by the way, would have been of exceptional interest.

The Principal, Vice-Principal, and Sir William Osler, who had promised to speak at the banquet, are in Europe, as well as many of our staff. Their return is uncertain.

THE CHEMICAL NEWS.

VOL. CX., No. 2860.

(STUDENTS' NUMBER).

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must either have passed the Matriculation Examination in this University, or be admitted under the Statute which provides that the Senate may admit graduates of or persons who have passed the examinations required for a degree in other Universities approved by it. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, &c., are open to Women upon exactly the same conditions as to Men.

There are three Examinations for Matriculation in each year; commencing on the second Monday in September, January, and June (or July, as may hereafter be determined).

Every Candidate for the Matriculation Examination must apply to the Principal for a Form of Entry on or before August 20, which must be returned fourteen days before the commencement of the September Examination; or must apply for a Form of Entry on or before November 25, which must be returned on or before December 1, for the January Examination; or must apply for a Form of Entry on or before April 25, which must be returned on or before May 1, for the June (or July) Examination; accompanied in each case by the proper Fee, and by a Certificate showing that the Candidate will have completed his Sixteenth Year on or before January 14 for the January Examination, July 31, the end of the Secondary School Year, for the June Examination, and September 15 for the September Examination.

Every candidate entering for the Matriculation Examination must pay a Fee of £2.

Intending Students (Internal and External) should obtain the "Regulations and Courses" from the Registrar, University of London, South Kensington, S.W.

Several valuable Scholarships and Exhibitions are available to students.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. H. Perkin, M.A., F.R.S.

Lees Reader in Chemistry—(Vacant).

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities and other persons suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, J. E. Marsh, M.A., F.R.S., N. V. Sidgwick, M.A., A. F. Walden, M.A., B. Lambert, M.A., F. D. Chattaway, M.A., D.Sc.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

There are also laboratories which specialise in different parts of the subject:—*Physical Chemistry*, Balliol and Trinity College Laboratory: D. H. Nagel, M.A., H. B. Hartley, M.A. *Inorganic Chemistry*, Christ Church Laboratory: A. Angel, M.A. *Quantitative Analysis*, Magdalen College Laboratory: J. J. Manley, M.A. *Jesus College Laboratory*: D. L. Chapman, M.A. F.R.S., *Queen's College Laboratory*: Rev. G. B. Cronshaw, M.A.

Scholarships of about the value of £80 are obtainable

at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—William J. Pope, M.A., F.R.S. *Jacksonian Professor of Natural and Experimental Philosophy*—Sir James Dewar, M.A., F.R.S.

Goldsmiths Reader in Metallurgy—Charles T. Heycock, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as a Student of Research, and obtain a degree after two years' residence in the University, by presentation of a thesis describing original research.

Facilities for research work are provided both in the Chemical Laboratories and in the Metallurgical Laboratories.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science at the several Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratories of the University are open daily for the use of the Students. The Demonstrators attend daily to give instruction. A list of the lectures and practical courses is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, from the *Cambridge University Calendar*, or from the "Students' Handbook to Cambridge."

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.

Professor of Applied Chemistry—Emil A. Werner, Sc.D., F.C.S., F.I.C.

Demonstrator—W. C. Ramsden, F.C.S.

Junior Demonstrator—H. Kall, B.A., B.Sc.

The general Quantitative and Research Laboratories include working accommodation for about 130 Students. The Laboratories will open on October 1st. Lectures will commence on November 4th.

The Laboratories and the Lectures of the Professor of Chemistry can be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The Lectures delivered are:—

1. *Inorganic Chemistry and Chemical Philosophy*.—Elementary, first year; Advanced Inorganic Chemistry, second year; Physical Chemistry, third year.
2. *Organic Chemistry*.—General, second year; advanced, third year.
3. *Metallurgy*.—A Course for Engineering and Technical Students.
4. *Agricultural Chemistry*.—Theoretical and Practical Courses.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The *Summer Course of Practical Chemistry for Medical Students* begins early in April and terminates about the middle of June.

A special course for Dental Students will be given.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Undergraduates, and tenable for five years. The Foundation Scholars receive £20 per annum, they have free commons, and their chambers for half the charge paid by other students; their tutorial fees are at one-fourth the usual rates.

KING'S COLLEGE. (UNIVERSITY OF LONDON).

Professors—Herbert Jackson, F.C.S., &c. (Daniell Professor), and A. W. Crossley, Ph.D., F.R.S., &c.

Assistant Professor—P. H. Kirkaldy, F.C.S., &c.

Lecturers and Demonstrators—S. W. Collins, B.Sc. L. E. Hinkel, B.Sc., A. W. Cremer, B.Sc., and H. V. Potter, B.Sc.

The Academical Year consists of Three terms. The days fixed for the commencement of Terms in 1914-1915 are Sept. 30, Jan. 13, and April 28.

The general Courses of Lectures on Chemistry deal with the nature and scope of the subject and the principles involved, in relating to one another the experimental facts, shown as illustrations of the properties of the elements and their chief compounds. The non-metallic elements are first treated of, as demonstrating most clearly the characters of the interactions between the different kinds of matter, and as affording the best opportunity of classifying the main groups of compounds met with, when dealing with the inorganic branch of the subject. The metallic elements and their compounds are then discussed, and this part of the Course is completed with a *résumé* in which the connected relations of the properties of the elements are described. The latter portion of the Course embraces in the same manner a study of the principles and properties of the carbon compounds which are examples of the main groups of organic substances. Class Examinations are held from time to time during the Session.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till five daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

For fuller details the separate Syllabuses provided for each class should be consulted.

UNIVERSITY COLLEGE. (UNIVERSITY OF LONDON).

Professors—J. Norman Collie, Ph.D., F.R.S. (Organic Chemistry); F. G. Donnan, M.A., F.R.S. (Inorganic and Physical Chemistry).

Assistants—S. Smiles, D.Sc.; Katharine A. Burke, B.Sc.; R. E. Slade, D.Sc.; W. B. Luck, D.Sc.; Irvine Masson, M.Sc.; H. Thacher Clarke, D.Sc.

The Session is divided into three Terms, as follows:—First Term, from October 5 to December 18; Second Term, from January 12 to March 26; Third Term, from April 27 to July 1.

Introductory Course of Inorganic Chemistry.

Tuesday and Thursday, at 11. Practical, Thursday, 2 to 3.30, or 3.30 to 5. Fee, £10 10s.

The principles of Elementary Inorganic Chemistry, illustrated chiefly by reference to:—Air, water, salt, ores, fuels, coal industry, furnace products, soda industry, mortar, cement, glass making, nitre and nitrogen-fixation; other technical processes, and the properties of metals.

Junior Course of Inorganic Chemistry.

The more important inorganic substances will be dealt with. Special attention will be paid to general points of view, and to the application of physico-chemical laws and methods.

First and Second Terms: The Class meets three times a week, on Mondays, Wednesdays, and Fridays, at 9, for Lectures, Examinations, and Exercises.

Third Term: Lectures will be given on Mondays and Fridays at 9 and another hour to be arranged.

Fees: Course, £7 7s.; First or Second Terms, £4 4s.

A Practical Class will meet throughout the Session.

Course of Physical Chemistry.

Tuesday and Thursday at 9.

A general Course on the Principles of Physical Chemistry and their applications.

Fee:—Course £5 5s.

Senior Course of Organic Chemistry.

Monday, Wednesday, and Friday, at 12, throughout the Session.

Fees:—For the Course, £6 6s.; for a Term, £2 12s. 6d.

An Advanced Course will be held twice a week throughout the Session for those engaged in prosecuting research in Organic Chemistry. Fee, £5 5s.; Term, £2 2s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Laboratories of General and of Organic Chemistry.

The Laboratories are open daily from 9 a.m. to 5 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Courses qualify Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. Several valuable Scholarships are available to students.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY.

Emeritus Professors—Sir W. A. Tilden, D.Sc., F.R.S., and Sir F. E. Thorpe, C.B., F.R.S., &c.

Professor and Director of the Chemical Laboratories.—H. Breton Baker, D.Sc., F.R.S., &c.

Professor of Chemical Technology and Fuel Chemistry.—W. A. Bone, F.R.S.

Professor of Organic Chemistry.—J. F. Thorpe, F.R.S.

Professor of Physical Chemistry.—J. C. Philip, M.A., D.Sc.

Assistant Professor.—B. Monat Jones, M.A.

The Imperial College of Science and Technology, incorporated under the Royal Charter of July 8, 1907, is an

institution or group of associated colleges with its principal seat at South Kensington.

The purposes of the Imperial College are to give the highest specialised instruction, and to provide the fullest equipment for the most advanced training and research in various branches of science, especially in its application to industry; and to do all and any of such things as the Governing Body consider conducive or incidental thereto, having regard to the provision for those purposes which already exists elsewhere.

For these purposes, the Governing Body, subject to the provisions of the Charter, are to carry on the work of the Royal College of Science, and the Royal School of Mines, and may establish Colleges and other Institutions or Departments of Instruction. Any Institution or Department so established, and, subject to the conditions of the Charter, the Central Technical College of the City and Guilds of London Institute, are to be integral parts of the Imperial College; and the Central Technical College is to be called and known in future as the City and Guilds College.

The Charter further provides that the Imperial College shall be established in the first instance as a School of the University of London. Students of the Imperial College who have matriculated at the University of London may therefore proceed to the Science degree of the University as "Internal Students."

Attention is particularly directed to the conditions of admission and to the extended facilities for Research Work.

The ordinary courses of instruction are planned so as to extend over four years, and are generally similar for all divisions during the first year, and to a less extent during the second year, after which they are specialised according to the particular course which the student is taking.

The following Diplomas have been awarded in the past to Students of the several constituent Colleges:—

The Associateship of the Royal College of Science (A.R.C.S.) in one or more of the following divisions:—Mechanics, Physics, Chemistry, Botany, Zoology, Geology. The Associateship of the Royal School of Mines (A.R.S.M.) in one or more of the following divisions:—Metallurgy, Mining.

The Associateship of the City and Guilds Institute, (A.C.G.I.) will be awarded in Engineering (Civil and Mechanical), Engineering (Electrical).

Twelve entrance scholarships are given in September each year, and post graduate scholarships are available for enabling fourth and fifth year students to complete their courses. Three Research Fellowships, founded by Mr. Otto Beit, of £150 a year, tenable at the Imperial College, are offered annually to post graduate students of this College, as well as to graduates of other Universities.

Full details can be obtained from the College Calendar, published by Eyre and Spottiswoode (or through any bookseller), price 6d.

THE SCHOOL OF PHARMACY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The 73rd Session will commence on Sept. 30, 1914.

Professors.—Chemistry, —; Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S. (Dean).

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry, Botany, Materia Medica and Pharmacy commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also of those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the Lectures and Practical Work in

Chemistry and in Botany are accepted as evidence of scientific training by the Institute of Chemistry in connection with the Examinations for the Associateship. Certificates of attendance at the Lectures and Practical Work in Chemistry are accepted by the Conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies. Certificates of attendance at the Course of Pharmacy are also accepted by the Conjoint Board.

Prospectuses and further information may be obtained from the Dean of the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

UNIVERSITY OF WALES.

Professor.—A. Findlay, M.A., D.Sc. (Aberdeen), Ph.D. (Leipzig), F.I.C.

Lecturer and Demonstrator.—T. Campbell James, M.A., Trinity College, Cambridge, D.Sc. (Wales).

Assistant Lecturer and Demonstrator.—C. R. Bury, B.A., B.Sc. (Oxon).

Lecture Assistant.—W. Beynon Williams, B.Sc.

Student Assistant.—Eric Walker, B.Sc. (Wales).

Lecturer in Agricultural Chemistry.—J. Jones Griffith, B.Sc. (Wales).

The College is open to men and women students above the age of sixteen years. The Session commences on Oct. 1st, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Intermediate Science Course; four lectures weekly throughout the Session. (2 and 3) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1914-1915, Course B). (4 and 5) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratories are open daily from 9 a.m. to 1 p.m. and from 2 to 6 p.m., Saturdays 9 a.m. to 1 p.m. Regular Courses of practical work, suitable for the B.Sc. degree of the Universities of London and Wales, or for the Associateship of the Institute of Chemistry, can be followed. Facilities are given for Students wishing to undertake research work. Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £17. This composition fee enables the Student to attend any or all the Classes and Laboratories of the College.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 16, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, K. J. P. Orton, M.A., Ph.D., F.I.C. Assistant Lecturers and Demonstrators, J. O. Hughes, B.Sc., Sybil M. Leslie, M.Sc., Lecturer in Agricultural Chemistry, H. E. Jones, B.A., B.Sc.

Physics.—Professor, E. Taylor Jones, D.Sc. Assistant Lecturers and Demonstrators, A. H. Ferguson, B.Sc. and W. E. Williams, B.Sc.

The Session opens September 29th, 1914. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £5.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 15s. Advanced Lectures on Organic Chemistry, £1 5s. Physical Chemistry, £1 5s.

Agricultural Chemistry.—Fee, £2 10s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 5 p.m. for instruction in Chemical operations and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; Composition Fee for all Lectures and Laboratory Classes of the Science Degree Course taken in one year, £16.

The College Courses are arranged with reference to the Degree Courses of the University of Wales (of which the College is one of the Constituent Colleges). The Courses in Science are also suited to the requirements of Students preparing for the Science Degree Course of the University of London.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and by the Conjoint Boards of the Royal Colleges of Surgeons and Physicians, and students can make one *Annus medicus* at the college. Students are prepared for the First Examination of the Universities mentioned, the First Examination for Medical Degrees of the University of London, and of the Conjoint Board of the Royal Colleges of Surgeons and Physicians. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES
AND MONMOUTHSHIRE, CARDIFF.

Professor of Chemistry—C. M. Thompson, M.A., D.Sc., F.C.S.

Assistant Professor—E. P. Perman, D.Sc., F.C.S.

Lecturer to Medical Students and Demonstrator—R. D. Avel, D.Sc., Ph.D., F.I.C., F.C.S.

Professor of Metallurgy—A. A. Read, D.Sc., F.I.C., F.C.S.

Assistant Lecturer and Demonstrator—R. H. Greaves, M.Sc.

The Session commences October 6th and terminates on June 25th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 30 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 10s.

The Intermediate Course consists of about 80 lectures; together with laboratory practice it forms the qualifying course for the Intermediate Examination of the University of Wales, and will cover the subjects required for the Intermediate Examination in Science (Part I.) of the University of London. Fee, £4 10s.

The Senior Course consists of about 80 lectures on Inorganic Chemistry; Fee, £3 15s.

A course on Organic Chemistry will be given in the Session 1915–1916.

In the laboratory each student works independently, so that the course of study may be adapted to the require-

ments of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £4 per session; eight per week, £6 6s. per session; twelve hours or more per week, £8 8s. per session.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

Students by making a payment of £16 at the commencement of each session may compound for all fees for the whole session.

At the entrance examination in April, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY OF BRISTOL.

DEPARTMENT OF CHEMISTRY.

Alfred Capper Pass Professor of Chemistry—Francis Francis, D.Sc., Ph.D., F.I.C.

Lecturers—O. C. M. Davis, B.Sc., D.Sc., F.I.C.; F. W. Rixon, M.Sc., Ph.D.

Lecturer in Physical Chemistry—James W. McBain, M.A., Ph.D.

Lecturer in Bio-chemistry—Max. Nierenstein, Ph.D.

Lecturer in Hygienic Chemistry—Edward Russell, B.Sc., F.I.C.

Lecture Assistant—J. H. Sturgess.

The session commences on September 29.

The Department of Chemistry is situated in the new wing of the University Buildings in Tyndall's Park, and was opened on October 1, 1910. The Department provides accommodation for 200 students, and laboratories for work in specialised branches of Chemistry have been designed and equipped with apparatus of the most modern type. All the laboratories are supplied with electric wiring for experimental purposes, and currents of any desired voltage up to 250 volts at 50 amperes from dynamo or storage cells may be obtained throughout the Department. Higher voltages and currents are available in special laboratories, for Physical Chemistry and Electro-metallurgy. Special facilities are afforded to those who desire to carry out research or to study Chemistry as applied to the different processes employed in the arts and manufactures; and a laboratory for Bio-chemistry has been specially designed for the investigations of problems on Biological lines.

DAY LECTURES.

General Courses.—1. General Inorganic Chemistry—Three lectures per week during Session and Laboratory work. 2. General Organic Chemistry—Three Lectures per week during one Session and Laboratory work. 3. Physical Chemistry—Three Lectures per week for first Session. Two Lectures per week for second Session and Laboratory work.

The Laboratories are open daily from 9.30 to 5 except on Saturdays, when they are open for Senior Students only.

Courses for Graduation.—*Intermediate Science*—Course 1 and one day Laboratory per week. *Pass Degree*—Course 2 and 3, and at least one day Laboratory per week during two Sessions. The Chemical Society must be attended during the second and third years, and one or more of the Special Courses arranged for Honours Students. *Honours Degree*—During the first year in the Honours School Courses 2 and 3, and the second and third, Course 3, and one or more of the following Special Courses as directed, e.g.:—Organic Chemistry, Physical Chemistry, Mathematical Chemistry, Advanced

Inorganic Chemistry, Applied Electro-chemistry, some part of Bio-chemistry.

The meetings of the Chemical Society must be attended during each Session.

Colloquium.—A weekly Colloquium will be held by members of the Staff to discuss recent advances in the various developments of Chemistry. Honours Students attend, and others interested are invited to do so.

Extract from Regulations as Regards Fees.

1. Registration Fee 7s. for a single Course; £1 rs. shall cover a perpetual registration for any number of Courses.

2. Inclusive Fee for an entire curriculum for degree of B.Sc., whether "Pass" or "Honours," shall be £21 a year.

3. The Fees for separate Courses of Lecturers in Faculty of Science shall be at the rate of £1 rs. per term, or £2 2s. a year for each hour per week for which the Course in question is offered.

The Fees for separate Laboratory practice and instruction in the Faculty of Science shall be at the rate of £2 2s. per term for each day in the week for which admission in the Laboratories is sought, with a minimum of £3 3s. in each particular case.

EVENING LECTURES.

The Laboratories are opened, for students who have attained the standard of an Inter. B.Sc. examination, from 6.30 to 9.30 p.m. on Tuesday during the Autumn and Spring Terms. Course 1 will be given on Wednesday at 8 to 9, and Course 2 or 3 on Friday at 8 to 9 p.m. during these Terms. The Lectures and Laboratory work in Course 1 will be similar to that given to Second year Students in the Faculty of Science, and that given in Course 2 or 3 to one of those given to Students studying or the Final Degrees in that Faculty.

Extract from Regulations as Regards Fees for Evening Students.

1. For Evening Students who enter on a curriculum for a Degree the Registration Fee shall be 5s., for a curriculum for a Certificate, unless the Student has matriculated, the fee shall be 10s. 6d.

2. Unless in any case otherwise prescribed, the Fees for Evening Classes in the Faculties of Arts and Science shall be 10s. 6d. for two terms, or for one term's attendance.

All communications to the University to be addressed to the Registrar. Information concerning Courses or Laboratory work in the Department of Chemistry may be obtained from the Professor.

The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, mining, or motor car engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the University into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the University. Several Scholarships are tenable at the University.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL. CHEMISTRY.

Professor—J. Wertheimer, B.A., D.Sc., F.I.C., F.C.S.

Lecturers—H. A. M. Borland, A.R.C.S.; Annie M. Herbert, B.Sc.

Demonstrators—E. G. Moody and F. L. Kitchin.

Assistant in Chemical Laboratory—W. Lewis.

In consequence of the foundation of the University of Bristol, the College now restricts its work to Applied Chemistry in the daytime; Pure Chemistry is taught in the Faculty of Science of the University of Bristol. The Engineering work of the late University College has, on the other hand, been transferred to this College.

The College Evening Classes commence on Monday, Sept. 21st.

Further detailed information may be obtained from the College Calendar, price 61., or the Prospectus for Day or Evening Classes (1d. each).

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., M.Sc., LL.D., F.R.S., F.I.C.

Assistant Lecturers and Demonstrators—Hamilton McCombie, M.A., Ph.D., B.Sc., A.R.C.S., A.I.C.; C. K. Linker, D.Sc.; J. E. Coates, M.Sc.; E. P. Frankland, Ph.D., B.A., M.Sc.

Professor of Metallurgy—Thomas Turner, M.Sc., A.R.S.M.

The Session will be opened on October 7th, 1913.

The Chemical Department has hitherto been housed in the new University buildings at Bournbrook, but owing to those buildings having been taken over by the Military Authorities for use as a Base Hospital the classes during the coming Session will be arranged for at the Birmingham Municipal Technical School and the Mason College.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Three hours weekly during the Winter and Spring terms. Mondays, Wednesdays, and Thursdays at 9.30 a.m. Fee, £4 4s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9.30 to 10.30 a.m. Fee, £1 11s. 6d.

Second Year.—**Advanced Organic Chemistry.**—This course extends over two years, and is divided into two parts:—(a) Carbon Compounds of the Fatty Series; (b) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. **Advanced Inorganic Chemistry.**—This course is devoted to the consideration of special branches of Inorganic Chemistry, and direction is also given as to the private reading which should be pursued by students. The class meets by arrangement once weekly during the Session. Fee, £1 rs.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A Course on Physical Chemistry. Fee, £2 2s.

Fourth Year.—For students preparing for the B.Sc. degree with Honours in Chemistry.

Special Courses in General Organic, and Physical Chemistry.

Practical Chemistry.

The instruction in Practical Chemistry extends over four years in the case of the Honours Degree. The Laboratory will be open daily from 9.30 to 5, except Saturdays, when it closes at 1 p.m. Fees—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms ..	13	8½	7½	5
Three Terms ..	18	12	11	6½

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee. Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

There is a separate University department for Metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in June.

Ascough Scholarship.—One Open Scholarship of the value of about £30 is awarded annually in July.

Bowen Scholarship.—One Open Scholarship in Metallurgy, value about £96, is awarded annually in June.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

CITY OF BRADFORD TECHNICAL COLLEGE.

Principal—Prof. W. M. GARDNER, M.Sc.

DEPARTMENT OF CHEMISTRY AND DYEING.

Professor of Chemistry and Dyeing—W. M. Gardner, M.Sc., F.I.C.

Assistant Professor of Chemistry—B. North, A.R.C.S. (Lond.).

Lecturers in Chemistry—L. L. Lloyd, Ph.D.; H. Middleton, M.Sc.; N. Bland, M.Sc.; A. Jackson, B.Sc.

Lecturer in Physics—J. A. Tomkins, A.R.C.S. (Lond.).

Demonstrator in Physics—F. Harcourt, B.Sc.

Lecturer in Dyeing—M. Fort, M.Sc.

Lecturer in Gas Manufacture—J. W. Roper.

Lecturer in Biology—J. A. Fisher.

The following courses of instruction are provided—

I. *General Chemistry Course*, extending over four years, and including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Electro-chemistry, Physical Chemistry, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry and Physics.

II. *Chemistry and Dyeing Course*, extending over four years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c. A completely equipped Practical Dyehouse and Finishing Rooms have now been added.

III. *Chemical Engineering*. Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Sanitary Science*. One year's Course, recognised by the Sanitary Institute as preparing for their certificate examination. Subjects: Chemistry, Physics, Sanitary Engineering, Sanitary Law, Building Construction, Drawing, Physiology, and Bacteriology.

V. *Dyeing*. Special Courses for Graduates in Chemistry, and for Drysalers, Colour Merchants, &c.

VI. *Textile and Dyeing*. Arranged for those Students who desire to study the two subjects simultaneously.

VII. *First Professional Examination, Conjoint Medical Board (M.R.C.S., L.R.C.P.)*, London.—Attendance at the College and College Certificates in Chemistry, Physics, and Biology are recognised by the Conjoint Board for Medical Studies as a qualifying curriculum.

VIII. *General Pharmaceutical Course*. Prepares for the Minor, Major, and Assistants' Pharmaceutical Examinations.

Each extends over two years on four half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Demonstrator—M. Kershaw, B.A., Ag.Dip. Cambs.

Assistant—H. Douglas Elkington, B.Sc., F.I.C.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

THE UNIVERSITY OF LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc., F.R.S.

Professor of Organic Chemistry—Julius B. Cohen, Ph.D., B.Sc., F.R.S.

Lecturer on Physical Chemistry—H. M. Dawson, D.Sc., Ph.D.

Assistant Lecturers and Demonstrators—W. Lowson, B.Sc., F.I.C.; W. H. Perkins, M.Sc., F.I.C.

Demonstrators—H. Calam, M.Sc., F.I.C.; J. Marshall, M.Sc.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £5 10s.
2. Advanced Inorganic Chemistry.—(A) Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £4 10s.
3. Advanced Inorganic Chemistry.—(B) Tuesday, Thursday, and Saturday, at 9.30 a.m. Fee, £4 10s.
4. Organic Chemistry.—Tuesday, Thursday, and Saturday at 11.30 a.m. Fee £4 10s.
5. Honours Courses—(a) Organic Chemistry: Monday, Wednesday, and Friday at 11.30 a.m.; fee, £4 10s. (b) History of Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the First Term; fee, £2 5s. (c) Physical Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the Second and Third Terms; fee, £3 7s. 6d. (d) Electro-chemistry: Tuesdays at 9.30 a.m.; £2 10s.
6. Chemistry of Food and Drugs.—Special class during the second term for Students taking Final Examination of the Institute of Chemistry in Branch E (Food and Drugs). £3 3s.

Laboratory Courses.

The University Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—£3 per half day of three hours per week.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 in the Second and Third Terms. Fee, £7 7s.

Tinctorial Chemistry and Dyeing Department.

Professor—Arthur G. Green, M.Sc., F.I.C.

Lecturer and Research Chemist—A. G. Perkin, F.R.S., F.I.C.

Assistant Lecturer—G. H. Frank, M.Sc., F.I.C.

The Courses extend over periods of three or four years, and are intended for those who wish to obtain a full scientific and practical education in the art of dyeing, colour manufacture, &c. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c., or in the manufacture of coal-tar products and dyestuffs.

Leather Industries Department.

Professor—E. Sullivan, Ph.D.

Assistant Lecturers and Demonstrators—Harold Brumwell; W. R. Atkin, M.Sc.

Demonstrator—F. C. Thompson, M.Sc.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Professor of Agricultural Chemistry—C. Crowther, M.A., Ph.D.

The full Course occupies three years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and outdoor agriculture at the University Farm.

Department of Coal-gas and Fuel Industries with Metallurgy.

Livesey Professor—J. W. Cobb, B.Sc., F.I.C.

Assistant Lecturer and Demonstrator—H. J. Hodsmann, M.Sc.

Research Chemist—W. Harrison, M.Sc.

The Courses extend over two, three or four years, and are suitable for those who are preparing for posts either as Gas Engineers or in Fuel and Metallurgical industries.

The Courses in Gas Engineering and the Technology of Fuel will chiefly deal with the manufacture and distribution of coal-gas and gas-lighting problems, by-product coking processes, and the production and application of gaseous fuels for heating and power purposes.

The Metallurgical Courses, besides dealing with general processes for the concentration and extraction of ores, will be chiefly directed to problems underlying blast furnace and open-hearth steel practice, and to the micro-structure, physical properties, and heat treatment of steel and other industrial alloys.

Research Students are admitted to the University Laboratories on reduced terms.

Several valuable Fellowships and Scholarships are at the disposal of the University, including a Fellowship of £200 offered by the Institution of Gas Engineers, and the Salt, Akroyd, Brown, Baines, Emsley, Craven, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The Leeds City Council's and the North, East and West Ridings County Council's Scholarships are tenable at the University of Leeds.

UNIVERSITY OF LIVERPOOL.

Professor of Inorganic Chemistry—E. C. C. Baly, M.Sc., F.R.S.

Professor of Physical Chemistry—W. C. McC. Lewis, M.A., Ph.D.

Professor of Biochemistry—Benjamin Moore, M.A., D.Sc., F.R.S.

Lecturer on Organic Chemistry—A. W. Titherley, D.Sc., Ph.D.

Lecturer on Metallurgy—G. D. Bengough, D.Sc., M.A., A.R.S.M.

Assistant Lecturers and Demonstrators—A. J. Allmand,

D.Sc.; C. S. Garrett, B.Sc.; Francis W. Kay, M.Sc., Ph.D.; A. Rule, D.Sc., Ph.D.; J. Smeath Thomas, M.Sc.

Lecture Assistant—H. H. Froyssell.

The Session commences October 7th.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in the University of Liverpool; for Degrees in Medicine of Liverpool; for the Pharmaceutical, Veterinary, Dental, and Public Health Diplomas; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry and other Examination Boards.

Lecture Courses.

A. General Introductory Course, including the principles of Organic, Physical, and Biochemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £6.

Pharmacy Courses: Junior, £3; Senior, £3.

Course B.—Inorganic Chemistry. Fee, £3.

Course C.—Inorganic Chemistry (Honours Course). Fee, £2 10s.

Course D.—Organic Chemistry. Fee, £3.

Course E.—Organic (Honours). Fee, £4.

Course F.—Physical Chemistry. Fee, £3.

Course G.—Honours Physical Chemistry. Fee, £4.

Course H.—History of Chemistry and Chemical Philosophy. Fee, £2.

Course J.—Applied Inorganic Chemistry, including Metallurgy. Fee, £2.

Course K.—Applied Organic Chemistry. Fee, £2 10s.

Course L.—Applied Electrochemistry. Fee, £2 10s.

Also Pass and Honours Courses in Biochemistry.

Research students carrying out research work pay a fee of £3 per annum.

The Inorganic and Organic Chemical Laboratories provide accommodation for every kind of work and research in inorganic and organic chemistry and in metallurgy. There is also a laboratory devoted to spectroscopic work and research.

The Muspratt Laboratories of Physical Chemistry and Electrochemistry adjoin the main chemistry buildings, and, owing to their full equipment, offer every opportunity or all manner of work and research in these subjects.

The Biochemical Laboratory is also separately housed, and provides facilities for work and research.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided. Fees:—

	One Term, Three Months.	Three Terms One Session
Per Week		
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week	10 10s.	21

D.P.H. Course (see special syllabus).

Course for Dental Degree and Diploma (see special syllabus).

Technological Curriculum.

The curriculum extends over three or four years.

The Final Examination for the Associateship of the Institute of Chemistry may be taken after the third year. Those students who have taken the Ordinary Degree of B.Sc. may pass the M.Sc. Exam. in any subsequent year.

The Sir John Willcox Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1913, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the Registrar not later than November 15. The Sheridan Muspratt Chemical Scholarship, on similar lines, is open for com-

petition. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes on Metallurgy will be held during the winter.

Prospectuses containing particulars may be obtained from the Registrar, University of Liverpool.

ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE. (IN THE UNIVERSITY OF DURHAM).

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., V.P.C.S., J.P.

Lecturers in Chemistry—F. C. Garrett, D.Sc., F.C.S., and J. A. Smythe, D.Sc., Ph.D., F.C.S.

Assistant Lecturers and Demonstrators—A. Foster, M.Sc., Ph.D., and J. B. Firth, M.Sc.

Demonstrators—A. S. Blatchford, B.Sc., and W. Wardlaw, B.Sc.

Lecturer in Agricultural Chemistry—S. Hoare Collins, M.Sc., F.I.C., F.C.S.

Assistant Lecturer in Agricultural Chemistry—A. A. Hall, M.Sc., Ph.D.

First Year Courses.—Division I.—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 7th. Fee, £3 10s. for the Session.

Division II. Similar to Division I, but modified to meet requirements of Students for Degrees in Engineering and Mining. Mondays 12 to 1, Tuesdays and Thursdays 10 to 11. Fee, £3 10s. for Session.

Second and Third Year Courses.—These lectures are designed to form a part of the course of instruction in Chemistry, and to prepare students for the examinations in Chemistry for the degree of Bachelor of Science, Pass and Honours.

(a) Inorganic Chemistry.—Advanced Course, Tuesdays and Thursdays at 11 a.m. Fees, Lectures, £3 10s. per session, and £1 10s. per term.

(b) Organic Chemistry.—Aliphatic and Aromatic Compounds, Tuesdays and Thursdays at 10 a.m. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(c) Organic Chemistry.—Advanced Course, Tuesdays and Thursdays at 12 noon for part of the session. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(d) History of Chemistry and Chemical Philosophy.—Saturdays at 10 a.m. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(e) Physical Chemistry.—Tuesdays and Thursdays at 12 noon for part of the session. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(f) Analytical Chemistry.—Fridays at 9 15 a.m. Fee, £1.

(g) The Rarer Elements and the Periodic Law.—Times to be arranged. Fees, Lectures, £3 10s. per session; £1 10s. per term.

Students taking Chemistry for Pass Degree will attend in their second year the courses *a* and *f*, and in their third year the courses *b* and *d*, in addition to the necessary Laboratory practice.

Students taking Chemistry for Honours Degree will attend in their second year the courses *a*, *b*, and *f*, and in their third year the courses *c*, *d*, *e*, and *g*, in addition to the necessary Laboratory practice.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9 15 a.m. Fee for the course, £1.

Metallurgy and Assaying.—Lecturer, Prof. Louis, M.A., D.Sc., F.I.C., F.G.S.; Demonstrator, H. Dean, M.Sc., A.R.C.M.; G. H. S. Kent. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working six days per week £5 10s. per term, £15 per session; one day per week, £2 per term, £5 per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the degree of Bachelor in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must have passed the University Matriculation Examination.

Matriculation Examination.—In order to enter on a course of study for a Degree a student must have previously satisfied the Examiners in the following subjects:—(1) English, (2) English History, (3) Mathematics, (4) three of the following subjects, of which one must be a language:—(a) Religious Knowledge, (b) Latin, (c) Greek, (d) Ancient History, (e) French, (f) German, (g) some other language to be approved, (h) Experimental Science or Physics or Chemistry, (i) Botany or Zoology, (j) Mechanics, (k) Extra Mathematics, (l) Geography.

(i.). Candidates for degrees in Arts, who do not offer Latin in their Matriculation Examination or in the equivalent accepted as exempting therefrom, will be required to pass in Latin at a subsequent examination before entering upon the Arts course.

(ii.). Candidates for degrees in Commerce, who do not offer a Modern Foreign Language in their Matriculation Examination, or in the equivalent as exempting therefrom, will be required to pass in a Modern Foreign Language at a subsequent examination before entering upon the Commerce course.

(iii.). Candidates for degrees in Engineering (Civil, Mechanical, and Electrical) and in Naval Architecture will be required to take the following subjects from the list:—(1) English; (2) English History; (3) one of four languages—Latin, Greek, French, German; (4) Experimental Science; (5) Extra Mathematics; (6) Geography.

(iv.). Foreign Students may be exempted from the Matriculation Examination on report from the Board of Professors of Armstrong College, that they have received such an education in their own country as will enable them to profit by University study, and that they have sufficient knowledge of English to enable them to follow the courses of instruction they are entering for.

For detailed Syllabuses and complete Regulations the College Calendar should be consulted.

Bachelorship in Science.—The degree of Bachelor of Science is conferred in Pass and Honours in Pure and Applied Science. For details of curricula, &c., the College Calendar should be consulted.

Exhibitions.—Two Exhibitions of the value of £20 and £10 respectively will be awarded in October next to

Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Thursday, October 1st, 1914. Candidates should send in their names to the Secretary on or before September 12th.

Evening Lectures.—Under the auspices of the College and the Newcastle Section of the Society of Chemical Industry, special Courses of Evening Lectures will be given—Course of 5 Lectures by Dr. J. W. Mellor, Fire Clays, to commence in October 1914, and a Course of 5 Lectures commencing January, 1915, to be announced later.

Several valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University; the examination for this Scholarship will be held during the week commencing October 6th. Candidates should send in their names to the Secretary on or before September 21st.

THE UNIVERSITY OF MANCHESTER.

Professor of Chemistry and Director of the Chemical Laboratories—Harold B. Dixon, M.A., M.Sc., Ph.D., F.R.S.

Professor of Organic Chemistry—Arthur Lapworth, D.Sc., F.R.S.

Reader in Biochemistry and Senior Lecturer in Chemistry—C. Weizmann, Ph.D., D.Sc.

Senior Lecturers and Demonstrators—Norman Smith, D.Sc.; E. C. Edgar, D.Sc.; and F. P. Bart, D.Sc.

Assistant Lecturers and Demonstrators—Edward Hope, M.Sc.; J. E. Myers, M.Sc.; W. J. Jones, M.Sc.; and J. R. Partington, M.Sc.

Professor of Metallurgy—C. A. Edwards, D.Sc.

Assistant Lecturer in Metallurgy—J. H. Andrew, M.Sc.

Lecturer in Electro-Chemistry—J. N. Pring, D.Sc.

The Session begins October 8th, 1914.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

This course is intended for Students commencing the study of chemistry.

Introduction to Organic Chemistry.—Mondays, Wednesdays, and Fridays, at 11.30, during the Summer Term.

This course is designed to meet the requirements of Students preparing for the Intermediate B.Sc. Examination.

Biochemistry, Theoretical and Practical.—Tuesdays and Thursdays during the Summer Term. This Course prepares for Part III. of the first M.B. Examination.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30, during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, and Fridays, at 2, during the two Winter Terms. The Metals.

Third Year Honours Course.—Theoretical and Physical Chemistry.

Organic Chemistry (General).—Mondays, Wednesdays, and Fridays, at 9.30, during the two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Thursdays, at 9.30, during the two Winter Terms.

History of Chemistry.—Short Courses during the two Winter Terms.

Chemistry of Colouring Matters.—Theoretical and Practical Course during the Winter Terms.

Metallurgy.—Inductory Course, followed by either—(A) Lead, Copper, Bismuth, Antimony, Zinc, and Tin; or (B) Iron and Steel. Course A, two Lectures per week during the first half of the Session. Course B, one Lecture per week during the Session.

Electro-chemistry.—General Theoretical Course: One hour per week during the Michaelmas and Lent Terms. Applied Course: One hour per week during Michaelmas and Summer Terms.

B.Sc. with Honours in Chemistry.—The course extends

over three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

The Research Laboratories for Inorganic, Organic, and Physical Chemistry, and for Metallurgy, are open to graduates and other advanced students.

For further particulars of any of these courses apply to the Registrar, Edward Fiddes, M.A., or to the Director of the Laboratories.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—R. M. Caven, D.Sc., F.I.C.; G. Sand, D.Sc.; and H. Lambourne, B.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student attends a course on Inorganic Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Brewing, Iron and Steel, and other Manufacturing Processes.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations.

The composition fee for full time in the Chemistry Department (lectures and laboratory) is £6 per term, and this fee covers all necessary apparatus and chemicals.

A composition fee of £6 per term is also charged for various complete courses, such as those required for the Institute of Chemistry, and for the degree examinations of London University.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, free from the Registrar.

THE UNIVERSITY OF SHEFFIELD.

Professor of Chemistry—W. P. Wynne, D.Sc., F.R.S.
Lecturers and Demonstrators—W. E. S. Turner, D.Sc., M.Sc.; W. J. Jarrard, B.Sc.; J. Kenner, Ph.D., B.Sc.; C. R. Young, B.Sc.

The Session will commence October 7th.

Matriculation Course.—Tuesday and Friday at 9.30. Fee, £2 12s. 6d., and three hours per week Laboratory work.

Candidates for the Intermediate Examination are required to satisfy the Examiners in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, and Botany. And those for the Final Examination in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, Botany, Physiology, Geology, Education.

Intermediate Course in Chemistry for B.Sc. or M.B.
Ch.B.—Monday, Wednesday, Thursday, and Saturday at 9.30 a.m. £5 5s., and six hours per week Laboratory work during first year.

B.Sc. Course in Chemistry.—Monday at 9.30 a.m. and Tuesday at 12.30 p.m. during second year, £3 3s.; Wednesday at 12.30 a.m., during two terms, Thursday at 10.30 a.m. and Friday at 10.30 a.m., during third year, £3 3s.; and nine hours per week Laboratory work during second and third years.

B.Sc. with Honours.—Honours Students in Chemistry, after passing the Intermediate Examination, devote the whole of their time to the study of Chemistry, and are expected to reach the standard for a pass in Chemistry for the ordinary degree by the end of the second year. During the second or third year they devote one day a week to lectures and practical work in a subsidiary subject—Mathematics, Physics, or Metallurgy—selected for the degree. The third year is devoted to the advanced study of Chemistry, either chiefly Physical and Inorganic or chiefly Organic, as the student may select. At least four days a week during the second and third years are spent in the laboratory.

M.Sc.—This degree may be conferred upon a Bachelor of Science with Honours who is of one year's standing from the date of his graduation as a Bachelor of Science, or upon a Bachelor of Science who has either passed an examination in an Honours School subsequent to graduation, or has for at least one year after graduation done research work at the University, and has presented a thesis, approved by the Faculty of Pure Science, upon the research work done during that period.

D.Sc.—The degree of Doctor of Science may be conferred upon any Master of Science of not less than five year's standing from the date of his admission to the degree of Bachelor, provided that he has published, in recognised journals or transactions, a research or researches of special merit and approved by the Faculty of Pure Science as qualifying him for the degree.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students.—Three hours per week, £3 3s.; Six, £5 5s.; Nine, £7 7s.; Twelve, £9 9s.; Eighteen, £12 12s.; Twenty-four, £14 14s.; Thirty-two, £16 16s.; Honour or University Students taking eighteen hours or more per week, £12 12s.

Students joining the Laboratory for one term are charged one-half, and for two terms two-thirds of the Fees for the whole Session.

A Course of Lectures, with a special class in Laboratory Work, is arranged for Medical Students entering for the Conjoint Board Examinations. Fee, £7 7s.

A course of Practical Chemistry which meets the requirements of candidates for the Diploma of Public Health is held during the Michaelmas and Lent terms. Fee, £6 6s.

An arrangement has been entered into with the Board of Education, London, S.W., which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Board being willing to pay the remainder under certain conditions, of which full information

may be obtained on application to the Registrar of the University.

Evening Classes.—Lecture Class and Laboratory, on Thursday evening during the Michaelmas and Lent terms. Fee, £1 10s.

DEPARTMENT OF METALLURGY.

Professor—J. O. Arnold, D.Met., F.R.S.

Senior Lecturers—F. K. Knowles, B.Met.; F. Ibbotson, B.Met., B.Sc.

Lecturer—J. H. Wreaks, B.Met.

Lecturer in Non-ferrous Metallurgy—G. B. Brook.

Lecturer in Electro-metallurgy—W. R. Barclay, A.M.I.E.E.

This Department has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of iron and steel, fuel, and refractory materials. It also contains a complete pyrometric installation, and a laboratory for the study of the micrographic analysis of metals fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The Department is now most complete for teaching the practical manufacture, the chemical constitution, and the physical properties of steel. Special attention is given to the determination of the microscopic constituents of steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected, but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates are granted only to those who follow the prescribed courses and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and on General Metallurgy. Practical Metallurgy.—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students in Collieries or Gas Works.

A steel works has been erected in connection with the Sheffield University at a cost of about £15,000, with a most varied and complete plant. The most recent addition to the steel works plant is a 3 cwt. Kjellin induction furnace worked by a 120 H.P. Motor-generator set with two-phase current. The Metallurgical Department of Sheffield University is "in association" with the Royal School of Mines for teaching the advanced metallurgy of Iron and Steel.

There has been recently added to the curriculum Day and Evening courses in Electro-metallurgy and Non-ferrous Metallurgy. The Electro-metallurgical Laboratory is completely equipped for the practical study of every branch of the art of the Electro-deposition of metals, special attention having, however, been paid—in the selection and arrangement of plant and apparatus—to the specific requirements of the Sheffield trades. The plant and machinery is thoroughly up-to-date in character. Working accommodation is provided for 30 students at one time, and the course extends over three university years.

The Non-ferrous Department has been established to meet the needs of the lighter Sheffield trades of Silver and Electro-plate, Brass, and allied industries. It is completely equipped for dealing with every phase of the work from the raw material. The melting shop is fitted with furnaces capable of dealing with casts up to 70 lbs. weight, so that commercial practice can be followed. Two large laboratories, the one with 32 places for preparatory students, the other with accommodation for 40 advanced students, provide the means for the Chemical examination of the alloys prepared. A Staff and Post graduate research laboratory completes the provision for the

chemical side of the work. The Micrographic Laboratory is equipped with a complete Zeiss Photo-micrographic camera, direct driven polishing blocks, and Ro's microscopes. The recalcination laboratory for the estimation of temperatures during melting, annealing, or other heat treatment has a complete pyrometric installation. An Arnold and Colver-Glauber Pyrometer permits of readings every 1° C. up to 1300° C. Facilities are provided for observing the thermal changes *in vacuo*. The Chronographic recorder is served by electric or coke furnaces, and the installation may be regarded as the most complete of its kind.

UNIVERSITY COLLEGE, READING.

Professor of Chemistry—H. Bassett, D.Sc., Ph.D., D.ès Sc., F.I.C.

Lecturers—J. W. Dodgson, B.Sc.; A. E. Everest, M.Sc.
Professor of Agricultural Chemistry—S. J. M. Auld, D.Sc., Ph.D., F.I.C.

Research Chemist in Dairying—J. Golding, F.I.C.

Lecturer in Agricultural Chemistry—J. A. Murray, B.Sc.

The lectures and laboratory work are so arranged as to be suitable for students preparing for the London B.Sc. (Pass or Honours), or for the College or other Diplomas in Agriculture, Horticulture, or Dairying. There is a general course of Intermediate standard, also another suitable for first year students of Agriculture and Horticulture. In their second and third years Science students attend special lectures in Inorganic, Organic, and Physical Chemistry, while Agricultural students take special courses under the Professor of Agricultural Chemistry. The laboratories are well equipped for all branches of practical work.

Halls of Residence—(Men) Wantage Hall, St. Patrick's Hall; (Women) St. Andrew's Hall, Wessex Hall, St. George's Hostel.

Full details of fees, scholarships, &c., can be obtained from the Registrar.

UNIVERSITY COLLEGE, DUNDEE.

UNIVERSITY OF ST. ANDREWS.

Professor of Chemistry—Alex. McKenzie, M.A., D.Sc., Ph.D.

Lecturer—J. K. Wood, D.Sc.

Demonstrator—S. C. Bate, B.Sc., A.I.C.

Lecture Assistant and Lab. Steward—J. Foggie, F.C.S.

The Session consists of three Terms:—The Martinmas Term begins early in October and ends before Christmas; the Candlemas Term begins early in January and ends about the middle of March; the Whitsunday Term begins in the middle of April and ends at the end of June.

Three Courses of Lectures are given, each extending through all three terms. The General Course, meeting four or five days a week (including Tutorial Meetings), is intended for beginners, and qualifies for Graduation Examinations in Arts (M.A. General), Science (First B.Sc.), and Medicine (First Professional).

The Special and Honours Courses, each meeting twice or thrice weekly, qualify for Degree Examinations in Arts (Special and Honours, respectively), and in Science (Final B.Sc. on Intermediate and Higher Standard, respectively).

All three are General Courses, including Inorganic, Physical, and Organic Chemistry.

The Laboratories are well equipped, and instruction is provided for students in Arts, Science (Pure and Applied), Medicine (including Public Health); provision is also made for students desiring to undertake Research.

UNIVERSITY OF ABERDEEN.

CHEMISTRY.

Professor—Frederick Soddy, M.A., F.R.S.

Lecturer on Physical Chemistry—Francis W. Gray, M.A., D.Sc.

Demonstrators—Joseph Knox, D.Sc.; W. H. T. Williamson, B.Sc.; James D. Pratt, M.A., B.Sc.

I. General Lecture Course (100 Lectures).—Daily during the Winter Session. The subjects treated or include (1) The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £4 4s.; for subsequent attendance, £3 3s. A Tutorial Class (without fee), conducted by the Junior Demonstrator, is held in connection with this course.

II. Physical Chemistry (60 Lectures)—Three Lectures a week on Physical Chemistry, with Practical Demonstrations, are delivered during the Winter Session by the Lecturer, Dr. F. W. Gray. Fee, £2 2s.

III. Inorganic Chemistry (40 Lectures).—Two Lectures a week on Advanced Inorganic Chemistry are delivered during the Winter Session by the Lecturer, Dr. J. Knox. Fee, £2 2s.

IV. Special Lecture Course on Organic Chemistry (50 Lectures).—Daily during the Summer Session. Fee, £3 3s.

V. Practical Course for Medical Students.—This course, which occupies five hours a week during the Summer Session—in all fifty hours—is devoted to practice in Elementary Qualitative Analysis. Fee, £3 3s.

VI. Chemical Laboratory.—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. The Course qualifies for the examinations of the Institute of Chemistry. Fee, £3 3s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

(The above arrangements are provisional only).

UNIVERSITY OF ABERDEEN AND ABERDEEN AND NORTH OF SCOTLAND COLLEGE OF AGRICULTURE.

Agricultural Chemistry.

Professor—James Hendrick, B.Sc., F.I.C.

Assistants—R. Glegg, B.Sc., F.I.C.; Ian G. Innes, M.A., B.Sc.

I. Preparatory Courses in General Chemistry and in Organic Chemistry are given for those who are unable to take the full University Courses in these subjects. The course in General Chemistry consists of about sixty Lectures with Practical Work (one hour daily) during the Winter Session. The course deals with the general principles of Chemistry, and with those parts of Inorganic Chemistry which are of more immediate concern to students of Agricultural Chemistry. The Practical Work goes along with and illustrates the Lectures. Fee, £4 4s.

The course in Organic Chemistry consists of about thirty Lectures, and is given during the Winter Session. It deals especially with those parts of the subject which are directly related to Agricultural Chemistry. Fee, £1 1s.

II. Agricultural Chemistry (General Course).—This class meets daily during the Winter Session, and includes both Lectures and Laboratory Work. The Lectures deal with the Chemistry of the Atmosphere, the Soil, Manures, Foods, Preservatives, Insecticides, &c. The Physiological Chemistry of Plants and Animals, the Composition and Manurial Requirements of Crops, and Dairy Chemistry are also treated of. The Laboratory Work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of Soils, Manures, Feeding-stuffs and Waters, and with the impurities and adulterations of these, occupy much of the time given to Practical Work. The fee for the whole Course (Lectures and Practical Work) is £4 4s.

III. Laboratory.—A Summer Course in Practical Chemistry is given to prepare students who have not previously done sufficient laboratory work for the course in Agricultural Chemistry. Fee, £2 2s.

IV. The Laboratory is open daily from 9 a.m. to 5 p.m. for students who wish to study the principles and practice of Agricultural Chemistry or to undertake research in this subject.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor—James Walker LL.D., D.Sc., Ph.D., F.R.S.
Lecturers—L. Dobbin, Ph.D.; A. C. Cumming, D.Sc.; W. W. Taylor, M.A., D.Sc.; and J. E. Mackenzie, Ph.D., D.Sc., and six Demonstrators.

The three working terms are each of ten weeks' duration, viz.:—Autumn term, October to December; Spring term, January to March; Summer term, April to June.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical students is given. The class meets daily; fee, £4 4s. The First Course for Arts and Science students meets three times a week throughout the year; fee, £4 4s. The Second Course is given on Organic, Advanced Inorganic, and Physical Chemistry. The class meets three times a week throughout the year; fee, £4 4s. Tutorial Classes are held in connection with the First and Second Courses. All Arts and Science Classes are open to Women Students.

In addition to the above, Advanced Lecture Courses are given on particular branches of Physical, Organic, and Inorganic Chemistry.

Laboratories.—Practical classes for Medical Students meet during the Winter Session and in the Summer Session. (Fee, £3 3s.). The Elementary Laboratory course for Arts and Science students is held for four hours per week during the year. Fee, £4 4s. The advanced laboratories for Science and Arts Students engaged in analytical and advanced practical work are open daily from 9.30 till 4.30. Fees: Whole Day—Year, £16 16s.; one term, £6 6s. Half Day—Year, £8 8s.; one term £3 3s. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry (including Gas Analysis, Physico-chemical Measurements, and Assaying). Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical language, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (i.e., Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination in Pure Science includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy (including Anthropology), Physiology, Geology (including Mineralogy), Zoology (including Comparative Anatomy), and Botany (including Vegetable Physiology). In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic Chemistry, Organic Chemistry, and Physical Chemistry. Practical Examination:—Complex Qualitative Analysis; Preparations; Gravi-

metric and Volumetric Analysis; Testing of Organic Substances. Each candidate taking the higher standard will also be examined on Ultimate Organic Analysis; Gas Analysis; Assaying; and Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.

Assisted by the following Lecturers and Demonstrators:—A. Archibald Boon, B.A., D.Sc.; Andrew King, F.I.C.; F. D. Miles, B.Sc.; and Clerk Ranken, D.Sc.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

An extensive range of new Chemistry Laboratories, embodying the most modern developments in laboratory design and equipment, and including a complete plant for the production of liquid air, has recently been built. The Chemistry Courses are designed to meet the requirements of Analytical and Technical Chemists. The College is a recognised training centre for the examinations of the Institute of Chemistry, and students can obtain the necessary instruction in General Chemistry, and also the specialised instruction required for the Final Examination for the Associateship of the Institute in the departments of Organic Chemistry, Metallurgy, Foods and Drugs, and Bio-chemistry.

The course for the Diploma of the College has been laid down on the same general lines as that required for the examinations of the Institute of Chemistry.

The Chemistry Courses are recognised by the University of Edinburgh as qualifying courses for the B.Sc. degree.

A Laboratory, under the charge of Prof. Emil Westergaard, has been provided for the study of Technical Mycology of Brewing, Distilling, Yeast Manufacture, Making Butter, Margarine, and Cheese Manufacture, Agriculture, Starch, Sugar, Preserve Making, &c. In this laboratory provision is made for the teaching of Biology, and the microscopic examination of Foods and Drugs, in connection with the examinations of the Institute of Chemistry.

Day Classes open on October 13th, and the Evening Classes on October 1st.

Matriculation Fee, 5s.; Composition Fees from £15 15s. to 21 guineas per annum. Full particulars are published in the Calendar of the College, which is issued early in September.

THE ROYAL TECHNICAL COLLEGE, GLASGOW.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A., LL.D., F.I.C.

Professor of Technical Chemistry—T. Gray, D.Sc., Ph.D.
Lecturer on Dyeing—A. B. Steen, B.Sc.

Lecturer on Sugar Manufacture—T. H. P. Heriot, F.C.S.

Professor of Metallurgy—A. Campion, F.I.C., F.C.S. Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

Session opens September 23rd, 1914.

The main object of this College is to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade. It was founded by an Order in Council, dated November 26th, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College (established 1796), the Young Chair of Technical Chemis-

try in connection with Anderson's College, the College of Science and Arts, Allan Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments. The diploma course in Chemistry extends over four years.

Students who have matriculated at the University of Glasgow can qualify for the degree of B.Sc. in Applied Science by attendance on the Day Classes of the College.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1914-1915 may be had from the Director, Mr. H. F. Stockdale,; price by post, rs. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD
Professor of Chemistry—James C. Irvine, Ph.D., D.Sc.

The Session begins on October 12th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about thirty-seven Bursaries, ranging in value from £50 to £10 each per annum, will be held on September 11th and following days. Twenty-two of these Bursaries are restricted to Men, one is open to Men or Women, and fourteen are restricted to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree, and the M.B., Ch.B. Degrees; the regulations will be found in the "University Calendar."

Lecture Courses.

Three distinct Courses of Lectures are given, each extending over the three terms of the academic year.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Exams., so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Final Science Exam. on the Lower Standard and the Special Exam. for the M.A. Degree.

Third Year's Course.—Short courses of lectures on selected topics are given to Students preparing for the B.Sc. on the Higher Standard or the M.A. Degree with Honours.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £4 4s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Practical Physical Chemistry. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the Exams. in Arts Science, and Medicine.

The fee for the Ordinary Course of Practical Chemistry is £3 3s., and for the Advanced Course £10 10s.

Original Research.

A special Research Department has been instituted by the University, the laboratories of which are open to students who give proof of their capacity to conduct original investigation. Graduates of other Universities who spend two years in the laboratory as Research Students are eligible for the D.Sc. degree of the University, and special chemicals and apparatus are provided free of charge. Graduate workers can also qualify for the Berry, 1851 Exhibition, and Carnegie Research Scholarships or Fellowships.

Students may work either independently or in collaboration with the Professor, to whom all communications should be addressed.

QUEEN'S UNIVERSITY, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.U.I., &c.

Lecturer on Organic Chemistry—A. W. Stewart, D.Sc.

I.—Chemistry.—The lectures are delivered at 12 o'clock on the first five days of each week, and terminate about the end of March. The course embraces the elements of Physical, Inorganic, and Organic Chemistry. Fee, £3 3s.

II.—Advanced Chemistry.—Inorganic and Organic. The lectures are given at such days and hours as suit the convenience of the class. Fee, £2 2s.

III.—Practical Chemistry.—In this course the Students are instructed in the general methods of Qualitative and Quantitative Analysis, Inorganic preparations, &c. The class is held on four days in the week during the second term for two hours each day. Fee, £3 3s.

IV.—Practical Chemistry for Engineering Students.—A special course is given during the third term. Fee, £3 3s.

V.—Laboratory Pupils.—The Chemical Laboratories are open from the second week in October to the beginning of July, on the first five days of the week, from 10 a.m. to 5 p.m. (except during the vacations). Students are admitted as working pupils on payment of a fee of £3 3s. for one term, £5 5s. for two, or £7 7s. for the whole Session. Facilities are provided for Students who wish to undertake research work.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Post Graduate Scholarships in Chemistry alone awarded annually of £50, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150, tenable for two or under special conditions for three years, and also one of the Industrial Bursaries.

UNIVERSITY COLLEGE, CORK.

A CONSTITUENT COLLEGE OF THE NATIONAL UNIVERSITY OF IRELAND.

Professor—Augustus Edward Dixon, M.D.

Assistant Lecturer—John Taylor, M.Sc.

The College Session will commence in October, 1914,

and end in June, 1915. All classes are open to male and to female students.

The following courses are provided:—

1. First Year Course for B.Sc.—General and Elementary Physical Chemistry, Inorganic Chemistry, Introductory Organic Chemistry, Practical Chemistry.
2. Second Year Course for B.Sc.—Advanced Inorganic Chemistry, Advanced Organic Chemistry, Practical Chemistry.
3. Third Year Course for B.Sc.—Physical Chemistry, Advanced Organic Chemistry, Practical Chemistry.
4. Courses in Systematic and in Practical Chemistry for students of Medicine proceeding to the Degrees of the University, or to the Examinations of the Medical Licensing Bodies of Dublin and of Edinburgh.
5. Courses in Systematic and in Practical Chemistry for Students of Engineering.
6. Laboratory Practical Course for the Diploma in Public Health.

Full particulars as to Lectures, Fees, Scholarships, Exhibitions, &c., are contained in the Regulations extracted from the College Calendar, which will be supplied on application to the Registrar.

NATIONAL UNIVERSITY OF IRELAND.

UNIVERSITY COLLEGE, GALWAY.

Professor—Alfred Senior, Ph.D., M.D., D.Sc., F.I.C., F.C.S., M.R.I.A.

Demonstrators—Robert B. Forsier, Ph.D., and Miss R. Clarke, B.A., B.Sc.

The Session commences in September and ends in June.

Faculty of Science.—1. *First Year's Courses.*—Laboratory: Inorganic preparations, simple quantitative and simple qualitative determinations. Lectures: A study of the chief non-metallic elements, their reactions and compounds, the molecular and atomic hypotheses, the leading metals, and an elementary consideration of the constitution and reactions of typical fatty and aromatic organic compounds. 2. *Second Year's Courses.*—Laboratory: Organic preparations, complex qualitative and quantitative inorganic determinations. Lectures: Advanced inorganic and organic chemistry. 3. *Third Year's Courses.*—Laboratory: Qualitative and quantitative organic determinations, molecular weight determinations, gas analysis, thermo-electro and photo-chemical and other physical determinations. Lectures: General, physical, inorganic, and organic chemistry, a detailed study of special branches, and the historical development of chemistry.

Faculty of Arts.—*First Year's Course.*—Same as Faculty of Science.

Faculty of Medicine.—*First Year's Courses.*—Laboratory: Same as in Faculty of Science, but less detailed, and including the detection of the chief alkaloids, glucosides, and carbohydrates. Lectures: Same as in Faculty of Science, first year.

Faculty of Engineering.—*First Year's Courses.*—Laboratory: Same as in Faculty of Science, but less detailed, and including a special study of metals, alloys, and other materials used in building construction, also determination of hardness in waters. Lectures: Same as in the Faculty of Science, but not including organic chemistry.

The College offers a Scholarship in Chemistry for competition in alternate years of the value of £60, and Chemistry enters into the subjects required for numerous Scholarships in the Faculties of Science, Medicine, and Engineering. The Royal Commissioners for the Exhibition of 1881 offer every two years a Science Research Scholarship of £150 per annum. This Scholarship has already been held by six Chemistry Students of this College.

For details as to Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar and other College publications may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Engineering (Mechanical and Electrical), Applied Chemistry, and Agriculture. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Applied Chemistry is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Inorganic Chemistry, Elementary and Advanced; (2) Organic Chemistry, Elementary and Advanced; (3) Analytical and Experimental Chemistry; (4) Physical Chemistry; (5) Metallurgical and Technological Chemistry and Assaying; (6) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. Assaying—£5 for three months; £9 for six months. £12 for the entire session.

There are six Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for three years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College.

A limited number of Scholarships in Science and Technology are competed for each year. These Scholarships are of the value of £50 a year for four years, and, in addition, entitle the holder to free instruction during the full Associateship Course.

For further particulars apply to the Registrar.

PROFESSIONAL CHEMICAL QUALIFICATION

(F.I.C. AND A.I.C.).

THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.—The Institute of Chemistry was founded in October, 1877, and incorporated by Royal Charter in June, 1885, to maintain the efficiency and integrity of the profession of Chemistry, including professional consulting and technological chemists, public analysts, and chemical advisers. *The Studentship.*—Every Candidate for admission to the Studentship is required to produce evidence that he is at least seventeen years of age, and that he has passed a Preliminary Examination in subjects of general education, recognised by the Council of the Institute. He must also show that, at the time of making application for registration, he is working at a College or University recognised by the Council, or under the direction of a Fellow of the Institute in an approved laboratory. *The Intermediate Examination in General Theoretical and Practical Chemistry.*—Candidates for admission to the Intermediate Examination (Fee, £5 5s.) are required to produce evidence (I.) of having passed an approved Preliminary Examination in subjects of general education; (II.) of having regularly attended systematic day courses, in a College or University recognised by the Council, during at least three academic years, in theoretical and practical Chemistry, and courses in Physics, Elementary Mathematics, and one of the following subjects, in accordance with the Regulations of the Institute: (i.) Higher Physics; (ii.) Advanced Mathematics; (iii.) Mechanical and Chemical Engineering; (iv.) Metallurgy; (v.) Geology and Mineralogy; (vi.) Physiology; (vii.) Bacteriology; (viii.) Agriculture; (ix.) Elementary Botany; (x.) Elementary Biology; and (III.) of having satisfactorily passed the Class Examinations in all the subjects required to be taken. As an alternative in the matter of training (II.), a candidate may take two years' day courses in a recog-

nised Institution as indicated above, and work systematically for two other years under a Fellow of the Institute in an approved laboratory. A Candidate who has taken a Degree in Science (including Inorganic and Organic Chemistry, and Physics in the Degree Examination, Mathematics having been also taken at either the Final or Intermediate University Examination) in a University recognised by the Council, is eligible for admission to the Intermediate Examination of the Institute. Holders of certain Honours Degrees or Diplomas are exempt from passing the Intermediate, and, by virtue of their qualifications, are eligible for admission to the Final Examination direct. A Candidate who has passed the Intermediate Examination of the Institute, or who is entitled to claim exemption from passing the Intermediate Examination, is eligible for admission to the Final Examination. *The Final Examination (Fee, £5 5s.) for the Associateship (A.I.C.).*—This comprises, in addition to a general knowledge of all branches of chemistry, a thorough knowledge of one branch—Mineral chemistry; metallurgical chemistry; physical chemistry; organic chemistry; chemistry (including microscopy) of food and drugs, fertilisers and feeding-stuffs, soils, and water; or biological chemistry. All Candidates for the Final Examination are required to translate French and German technological literature, with the aid of dictionaries. Candidates taking the food and drugs section must take a course in botany, and those taking biological chemistry a course in biology. *Fellowship (F.I.C.).*—For admission to the Fellowship, an Associate is required to have been registered for three years, and to have been continuously engaged during that period in the study and practical work of applied chemistry in a manner satisfactory to the Council.

Full particulars are given in "The Book of Regulations for the Admission of Students, Associates, and Fellows," which may be obtained (gratis) from the Registrar, 30, Bloomsbury Square, London, W.C. Past Examination Papers, Annual Sets, 6d. each.

The Institute will probably remove to 30, Russell Square towards the close of 1914.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE.—The operations of the Institute are divided broadly into four branches:—(1) The City and Guilds (Engineering) College, (2) the City and Guilds Technical College, Finsbury, (3) the City and Guilds South London Technical Art School, and (4) the Department of Technology of the Institute. Programmes of the London Colleges may be had on application to the Temporary Offices during the rebuilding of Gresham College, Leonard Street, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. The Programme of the College, containing full particulars of the conditions of entrance, fees, and courses of instruction, may be had on application. *City and Guilds (Engineering) College, Exhibition Road.*—The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of

the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons training to become Technical Teachers; 2. Persons preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in the various special subjects. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting.

CITY OF LONDON COLLEGE, White Street, Moorfields.—I. S. Scarf, F.I.C., F.C.S., and Assistants. Classes and Laboratory Practice in Chemistry, Botany, and Geology, open to Students of both sexes. Courses on Commercial Products—Oils, Butter, Tea, Timber, Textiles. Session commences Sept. 28.

THE POLYTECHNIC, Regent Street, W.—Frank E. Weston, B.Sc., F.C.S., and Assistants. General, Technical, and Applied Chemistry. Gas Manufacture and Analysis, Oils and Fats, Dairy Products, Conjoint Board Chemistry, Chemistry for Insurance Surveyors. Session commences Sept. 28.

BATTERSEA POLYTECHNIC.—Principal, S. G. Rawson, D.Sc., F.I.C. Inorganic, Organic, and Technological Chemistry, John Wilson, M.Sc. (Vit.), F.I.C., and Assistants. Complete courses of instruction are given in Chemistry (Inorganic and Organic), together with Physics, Electricity, Engineering subjects, Analysis of Foods, Bacteriology, Materia Medica, Paper Making and Testing, Oils and Fats, Toilet Soap Manufacture, Dyeing and Cleaning, &c., for intending technological and works chemists. Certain of the Courses (Day and Evening) are recognised by the University of London in preparation for the B.Sc., for which examination (Pass and Honours) complete courses of instruction, under recognised teachers, are provided. Special Evening Courses in various Technical subjects. (For further information see College Calendar).

BOROUGH POLYTECHNIC INSTITUTE, 103, Borough Road, S.E.—Chemistry Department under the Direction of C. Dorée, M.A., D.Sc. Evening Lectures and Laboratory Work in Inorganic and Organic Chemistry. Special Lectures and Laboratory Courses in Electrochemistry and Electro-chemical Analysis. Special Courses of Lectures on various Technical subjects. (For further information see College Calendar).

BIRKBECK COLLEGE, Breams Buildings, Chancery Lane.—Chemistry Courses conducted by G. Senter, D.Sc., Ph.D., (assisted by G. W. Clough, B.Sc., F. Barrow, M.Sc., G. Martin, M.Sc., and F. W. Snelgrove, B.Sc.) prepare for various Examinations, the B.Sc. and M.B. Degrees of the London University, Conjoint Board, Pharmaceutical Examinations, Board of Education, &c. The Session will commence on Friday, Sept. 25. The Day and Evening courses of study include Chemistry, Physics, Botany, Zoology, Geology, Mathematics, Latin, Greek, Modern Languages, Economics, Geography, Logic, History, and various branches of Law. All the Courses are conducted by recognised teachers of the University and provide for the Examinations of the University of London. The Calendar supplies detailed information respecting the Courses of Study, Examinations, &c.

NORTHERN POLYTECHNIC INSTITUTE, Holloway Road, N.—Principal, R. S. Clay, D.Sc. Instruction in theoretical and practical Inorganic and Organic Chemistry. Systematic Day and Evening Courses for the London University Degrees, Pass and Honours, also for the Board of Education examinations. Prospectus sent free on application to the Secretary.

NORTHAMPTON POLYTECHNIC INSTITUTE, St. John Street, E.C.—Principal, R. Mullineux Walmsley, D.Sc., &c. Classes in Electro-chemistry, Electro-plating, Electro-metallurgy, Electrotyping, Stereotyping, and Metal Colouring. (For full details see Prospectus).

SOUTH WESTERN POLYTECHNIC INSTITUTE, Manresa Road, Chelsea.—This Institute offers facilities for academic and technical education in many branches of Chemistry and Metallurgy. The department has designed both day and evening courses to meet the many requirements of these professions in London. Complete courses in General Chemistry, Metallurgy, and Assaying requisite for the B.Sc. and A.I.C. Examinations, Technical Courses. Ample opportunity for individual work has been arranged for both day and evening students. A full list of these courses will be supplied on application. A feature of the laboratory work is the facility given for specialising in any particular branch of the above subjects, thus supplying a much-needed want to men who have neither the time nor necessity for attending a degree course. The various lecturers will be pleased to advise intending students with regard to selection of courses. The department is under the control of J. B. Coleman, A.R.C.S., A.I.C., F.C.S., and the wish of the Institute is to make its courses of sound practical use to those engaged in Chemical Industries.

EAST LONDON COLLEGE, Mile End Road, E.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D., F.R.S.

SIR JOHN CASS TECHNICAL INSTITUTE, Jewry Street, Aldgate.—Principal, Charles A. Keane, D.Sc., Ph.D., &c., assisted by R. S. Willows, M.A., D.Sc., H. J. S. Sand, D.Sc., Ph.D., G. F. Morrell, B.Sc., Ph.D., &c., Arthur R. Ling, F.I.C., C. O. Bannister, A.R.S.M., M.I.M.M., G. Patchin, A.R.S.M., Wesley J. Lambert, Assoc. Inst. C.E., Arthur Harden, D.Sc., F.R.S., &c., J. S. S. Brame, E. C. Snow, M.A., D.Sc., F. J. Halow, B.Sc., &c. The new Session of the Sir John Cass Technical Institute, which is especially devoted to technical training in Experimental Science and in the Artistic Crafts, will commence, as originally arranged, on Monday, September 21st. The instruction in experimental Science provides systematic courses in Mathematics, Physics, and Chemistry for London University examinations in addition to the courses on higher technological instruction, which form a special feature of the work of the Institute. In connection with the latter, several new departures are being made for the coming Session. The curriculum in connection with the Fermentation Industries has been much developed, and now includes courses of instruction on Brewing and Malting, Bottling and Cellar Management, Brewery Plant, and on the Micro-biology of the Fermentation Industries. A connected series of lectures dealing with the Supply and Control of Power has also been arranged to meet the requirements of those engaged in works connected with Chemical, Electrical, and the Fermentation Industries. These will comprise a course of 20 lectures on the Supply and Control of Liquid, Gaseous, and Solid Fuel, a course of 5 lectures on Electrical Supply and Control, and a connected course of 5 lectures on the Transmission of Power. In the department of Physics and Mathematics, a special course of Lectures and Demonstrations will be given on Colloids, which will deal with the methods employed in their investigation and their relation to technical problems; also special courses of Lectures on the Influence of Surface Tension on Chemical Phenomena, the Construction and Uses of Physical Instruments in their Application to Physical Chemistry, the Methods of Dif-

ferential and Integral Calculus, and on the Theory and Application of Mathematical Statistics, the latter of which will treat of the application and modern mathematical methods of dealing with statistical data in social, educational, economic, and physical problems. Opportunity will be given to students to investigate problems on their own account. In the Metallurgy department, in addition to the ordinary courses of instruction in general Metallurgy, special courses of an advanced character are provided on Gold, Silver, and allied metals, on Iron and Steel, on Metallography and Pyrometry, on Heat Treatment of Iron and Steel, on Mechanical Testing of Metals and Alloys, on Mining, Mine Surveying, and on Mineralogy.

EAST HAM TECHNICAL COLLEGE.—Principal, W. H. Barker, B.Sc. Head of Chemical Department—A. E. Dunsan D.Sc. (Lond.). Lecturers—F. B. Thole, D.Sc.; E. D. Griffiths, B.Sc.; R. W. Wilson, F.C.S. Demonstrators—S. J. Plaise; A. G. Mussell. Chemical Engineering and Gas Engineering—A. J. Nice. Gas Supply—G. Jenkins. Soap Manufacture, and Oils, Fats, and Waxes—H. Appleton. Tar Distillation, &c.—A. J. Nice and A. E. Dunsan, D.Sc. Metallurgy—F. B. Thole, D.Sc. Sugar Manufacture—A. Wade. Painters' Oils, Colours, and Varnishes—R. A. Phillips. Evening Classes and Secondary School.

BLACKBURN MUNICIPAL TECHNICAL SCHOOL.—Chemistry: Robert H. Pickard, D.Sc. (Lond.), &c., assisted by Jos. Yates, M.Sc., F.I.C., Jos. Kenyon, B.Sc., F.I.C., and Hannah de Pennington, B.Sc. Session commence Monday, Sept. 28. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d., by post 3d.).

REDRUTH SCHOOL OF MINES (now incorporated in the School of Metalliferous Mining, Cornwall).—Complete courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Assaying, Mineralogy, Blowpipe Analysis, Mine Surveying, Geology, Principles of Mining, Ore Dressing, Mechanical Engineering, &c., for intending Assayers, Mineral Chemists, Mining Engineers, and Surveyors. Practical instruction in Mining given at the Basset Mines, Ltd. Syllabus on application.

MUNICIPAL SCHOOL OF TECHNOLOGY, Sackville Street, Manchester.—Laboratories and workshops for Mechanical, Electrical, Sanitary and Hydraulic Engineering, Textile Industries, Photography, Collotype and Photo-mechanical processes, Letterpress and Lithographic Industries, and industries within the scope of Architecture. The provision for the teaching of Chemistry, as might be expected in a district where the Chemical Industries are important, is of an exceptionally complete character. It comprises laboratories for Metallurgy, Brewing, Bleaching, Dyeing and Printing, Paper-making, and Electro-chemistry. The Bleaching, Dyeing, Printing and Finishing, and the Paper-making industries are in addition extensively equipped in a separate building with machinery and appliances on an industrial scale. A Brew-house is also equipped on the low gravity principle, with a plant of four bushel capacity.

WOLVERHAMPTON MUNICIPAL SCIENCE AND TECHNICAL SCHOOL.—Principal, J. D. Coales, D.Sc., M.I.E.E.; Inorganic and Organic Chemistry, Th. J. Murray, M.Sc., Ph.D.; Physics, A. T. Harrison, B.Sc.; Botany, Sidney Phillips, Ph.C. Human Physiology and Hygiene, H. J. Tench, A.R.S.I. Materia Medica and Pharmacy, F. W. Thompson, Ph.C. Day Classes in Chemistry, and Evening Classes in Chemistry, Physics, Botany, French, &c. Special arrangements are made for the requirements of Pharmaceutical and Medical Students and Chemical Trades. Session commences Monday, Sept. 14th. For other particulars and programme, apply G. F. Chell, Secretary.

MUNICIPAL TECHNICAL INSTITUTE, BELFAST.—Principal, F. C. Forth, A.R.C.Sc.I. Chemistry, Prof. H. Wien, M.A., Ph.D., D.Sc., and Assistants. Day and Evening Courses. Session opens Monday, August 31, 1914.

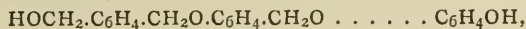
SYNTHETIC RESINS.*

By L. V. REDMAN, A. J. WEITH, and F. P. BROCK.

(Concluded from p. 131).

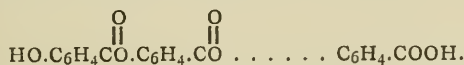
Reasons for Accepting the Chain Formula.

OXYBENZYL alcohol condenses by dehydration to a resin which yields, on combustion analyses, an empirical formula represented by $8(C_7H_5O_2 - 7H_2O$ or $11(C_7H_5O_2) - 10H_2O$ (Kraut, Beilstein, Seelheim, *loc. cit.*). This condensation is most easily represented by the chain constitution,—



and since the resin is soluble in caustic potash the hydroxyls are free as the formula indicates and not an inner anhydride. The close resemblance of the phenolmethylene condensation to the condensation of oxybenzyl alcohol is apparent.

The salicylate condensations which are closely allied to the dehydration of oxybenzyl alcohol pass, with the loss of water, to a resin represented by $9(C_6H_4OH.CO_2H) - 8H_2O$, which is most easily represented by a chain formula (Schroeder, Prinzhorn, and Kraut, *loc. cit.*),—



This resin not only dissolves in a solution of KOH, but is hydrolysed by it back into salicylic acid.

The fact that the soluble resin which we have named phenyl-endeke-saligeno-saligenin and which is similar to the resin which Dr. Baekeland calls novolak, and which we have shown to possess the probable formula $C_6H_5.(OCH_2.C_6H_4)_{11}OCH_2.C_6H_4.OH$ passes with the further absorption of methylenes to the insoluble resin, is the strongest argument in favour of the material being a chain molecule of indefinite length. If the resin novolak passes to the insoluble resin of greatest chemical inertness, tensile strength, &c., as we have ample proof that it does, then so large a molecule as novolak could not possibly pass to the final inner anhydride formula which Dr. Baekeland suggests for Bakelite C, unless the larger molecule previously hydrolysed into small aggregates, a reaction which is improbable. At best, the final resin formed from phenol and hexamethylenetetramine cannot be formed by the mechanism which Dr. Baekeland suggests for the formation of Bakelite C, which consists in the addition of CH_2O to a shorter chain to form an inner anhydride.

CH_2O is not and cannot be present in a reaction between anhydrous phenol and hexamethylenetetramine. If water be formed, which, later, decomposes the hexamethylenetetramine to form CH_2O , 2.7 per cent would be required to produce enough CH_2O for the above reaction to take place, and we have shown that the total by-products formed in this reaction are at least 99.5–99.7–100.0 per cent pure ammonia, leaving on an average about one-tenth of the water necessary for the reaction, *i.e.*, if our gross error in determining ammonia be considered as entirely due to the formation of water (a supposition which has little probability behind it).

A further reason for holding to the chain formula is from the fact that the final resins, whether formed from phenol and formaldehyde or hexamethylenetetramine, are slowly soluble in normal caustic potash. This fact points to the presence of a free hydroxyl in the molecule of the final resin. The hydroxyl may be removed or filled with groups which make the resin inert towards alkalis.

For the sake of completeness, the following tables of constants for these resins have been added :—

PHYSICAL AND DIELECTRIC PROPERTIES OF THE RESINS.

In the study of these resins for possible commercial uses the following constants have been determined :—

Tensile Strength.

The tensile strength of the pure resin is between 2000 and 4500 pounds per square inch, depending upon the conditions under which it is made, such as temperature, pressure, and time of heating.

The influence of temperature and time of heating upon the tensile strength are given in the following table :—

TABLE I.—Tensile Strength.

No.	Time heated Hours.	Temperature °C.	Tensile strength lbs per sq. in.	Aggregate average showing effect in time lbs per sq. in.
4.	½	123	1600	—
8.	½	146	1420	1646
12.	½	181	1920	—
5.	1	129	1900	—
9.	1	155	1540	2050
13.	1	179	2710	—
6.	1½	128	2000	—
10.	1½	150	2750	3050
14.	1½	181	4400	—
7.	2	127	1630	—
11.	2	150	3600	2716
15.	2	183	2920	—

By adding the values corresponding to a given temperature, the effect of temperature upon the tensile strength can be determined.

TABLE II.—Temperature.

Temperature °C.	Average total value in lbs. per sq. in.
125	2377
150	3103
180	3650

These values show that the higher the temperature at which the material is heated, the stronger it becomes in a given length of time.

The influence of the moulding pressure upon the tensile strength is shown in Table III.

TABLE III.—Moulding Pressure.

No.	Moulding pressure lbs. per sq. in.	Tensile strength lbs. per sq. in.
16.	2860	800
17.	5700	937
18.	8560	3200
19.	11,400	3970

The material used in these experiments consisted of a mixture of the rubbery product and the final product. It was desirable to know what mixture gave the highest tensile strength. The following table shows the influence of the composition upon the tensile strength :—

TABLE IV.—(Rubbery and Final Product). Tensile Strength.

No.	Per cent rubber product.	Final product.	Tensile strength lbs. per sq. in.
37.	10	90	4720
38.	20	80	4510
39.	30	70	2880
41.	50	50	2120

This table shows that it is best to use only a few per cent of the rubber product. This is to be expected since the rubber product by itself is comparatively brittle.

Crushing Strength.

The crushing strength of the resin is much higher than the tensile strength, which is usually the case with comparatively brittle materials, and varies from 20,000 to 30,000 pounds per sq. in. (ebonite 2200 and porcelain 15,000).

* Journal of Industrial and Engineering Chemistry, vi., No. 1.

Table V. gives the relation of the crushing strength, time of heating, and temperature of heating and tensile strength.

TABLE V.

No.	Tensile strength.		Time.		Temp. °C.	Crushing strength.	
	Lbs. per sq. in.		Hours.	Mins.		Lbs. per sq. in.	
4.	1600		0	30	123	7456	
10.	2750		1	30	150	20,800	
13.	2710		1	0	179	22,250	
14.	4400		1	30	181	28,100	
20.	2700		1	30	183	30,400	
24.	3100		1	30	184	32,000	

For higher temperatures than those given in the table there is no increase in strength in the resin and for temperatures above 300° C. the resin begins to weaken.

Dielectric Strength.

Discs of the resins half a millimetre thick gave voltage puncture tests of from 40,000 to 50,000 volts. These tests were made for us through the kindness of the Crocker-Wheeler Company. By way of comparison, hard rubber has a dielectric strength of 38,000 volts per millimetre and ebonite 30,000.

Specific Electrical Resistance.

The specific electrical resistance of the final resin as determined by the Bureau of Standards at Washington varies from 2.7 to 2800 × 10⁶ megohms per cc., depending upon the method of treating the same.

TABLE VI.—Specific Electrical Resistance.

No.	Heated in water-bath.		Heated in oven.	Tempera- ture of oven. °C.	Specific resistance. Megohms per cc.
	Hours.	Mins.	Hours.		
1.	17	0	5	154	73 × 10 ⁶
2.	22	30	10	164	2800 × 10 ⁶
3.	20	0	10	135	96 × 10 ⁶
4.	22	30	15	125	240 × 10 ⁶
5.	22	30	10	129	150 × 10 ⁶
6.	17	0	5	123	2.7 × 10 ⁶

The resins formed by the reaction between hexamethylene and phenol in the anhydrous state as described in this monograph present all the commercial possibilities of the resins formed in the water processes, and have certain other valuable qualities in themselves such as uniformity of product, ease of manipulation in the making, and higher dielectric properties than the wet formed resins containing traces of water and the condensing agents. The application of these anhydrous resins to the electrical, paint, varnish, lacquer, glue, moulding, and other industries has been so great as to require special treatment in a separate monograph.

Application for basic and process patents on these resins and their uses have been made by our firm, S. Karpen and Brothers of Chicago, who have given very hearty and liberal financial support to this multiple Fellowship in the Industrial Department of Kansas State University.

We wish to express our very deep thanks to Dr. R. K. Duncan, at whose kind suggestion and encouragement this research was undertaken and completed.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Pure Calcium Carbonate.—We should feel greatly obliged if you could give us the name of any good firms in England manufacturing pure white carbonate of lime in finest powder form. We have an enquiry for this product from one of our French manufacturers, and any information you are able to give us will be esteemed.—FENESTRE, CADISCH, and Co.

A SELECTION FROM MACMILLAN'S STANDARD BOOKS ON CHEMISTRY.

A COMPLETE TREATISE ON INORGANIC AND ORGANIC CHEMISTRY.

By the Right Hon. Sir HENRY ROSCOE, F.R.S.,
and C. SCHORLEMMER, F.R.S. 8vo. 8vo.

Vol. I. *The Non-metallic Elements*.—Fourth Edition, completely revised by the Right Hon. Sir HENRY ROSCOE, assisted by Dr. J. C. CAIN. 8vo. 21s. net.

Vol. II. *The Metals*.—Fifth Edition, completely revised and brought up to date by the Right Hon. Sir HENRY ROSCOE and others. 8vo. 30s. net.

. These two volumes together form a Complete and thoroughly up-to-date Treatise on Inorganic Chemistry.

Vol. III. *Organic Chemistry. The Chemistry of the Hydrocarbons and their Derivatives*.—Part II., 21s.; Part III., 18s.; Part IV., 21s.; Part VI., 21s.

A MANUAL of PRACTICAL PHYSICAL CHEMISTRY. By FRANCIS W. GRAY, M.A., D.Sc., Lecturer in charge of the Physical Chemistry Department, Aberdeen University. Crown 8vo. 4s. 6d.

A.M.A. CIRCULAR.—"This is one of the important books of the month. It contains much that is new, both in text and diagrams, and indications of important modifications in well-known experiments are numerous. . . . We cordially recommend this book to our readers."

A FIRST BOOK of CHEMISTRY. By W. A. WHITTON, M.Sc. Illustrated. 1s. 6d. [First Books of Science.]

FIFTH EDITION. Entirely Re-written and Enlarged.
VOL. II. JUST PUBLISHED.

CHEMICAL TECHNOLOGY AND ANALYSIS OF OILS, FATS, and WAXES.

By Dr. J. LEWKOWITSCH, M.A., F.I.C. Fifth
Edition, entirely Re-written and Enlarged. Edited
by GEORGE H. WARBURTON. In Three Vols.
Illustrated. Med. 8vo. Vol. I., 25s. net; Vol. II.,
25s. net.

FOURTH EDITION. Thoroughly Revised.

The PRINCIPLES of INORGANIC CHE-
MISTRY. By WILHELM OSTWALD. Trans-
lated by ALEXANDER FINDLAY, M.A., Ph.D.,
D.Sc., Professor of Chemistry and Director of the
Edward Davies Chemical Laboratories, University
College of Wales, Aberystwyth. Illustrated.
Fourth Edition. 8vo. 18s. net.

SCIENTIFIC FOUNDATIONS of ANA-
LYTICAL CHEMISTRY. By WILHELM
OSTWALD, Ph.D. Translated by G. MCGOWAN,
Ph.D. Third Edition. Crown 8vo. 6s. net.

OUTLINES of GENERAL CHEMISTRY.
By WILHELM OSTWALD, Ph.D. Third
Edition. Translated by W. W. TAYLOR, M.A.,
D.Sc. 8vo. 17s. net.

INTRODUCTION to PHYSICAL CHEMIS-
TRY. By JAMES WALKER, F.R.S. Sixth
Edition. 8vo. 10s. net.

LABORATORY NOTES on ORGANIC
CHEMISTRY for MEDICAL STUDENTS. By
PAUL HAAS, D.Sc., Ph.D. Crown 8vo. 2s. 6d.
net.

ST. GEORGE'S HOSPITAL GAZETTE.—"A distinctly
useful book. . . . In a university or a hospital which possesses
a good chemical laboratory this book should be invaluable."

MACMILLAN & CO., Ltd., LONDON.

THE CHEMICAL NEWS.

VOL. CX., No. 2861.

THE CAPTURE OF GERMANY'S CHEMICAL INDUSTRIES.

As has already been stated in the *CHEMICAL NEWS*, the manufacturers, and especially the manufacturing Chemists of this country, have a vital patriotic duty to perform at the present time; the manufacture of many articles which have hitherto been made chiefly in Germany, and the supply of which has been practically cut off by the war, is urgently necessary for the welfare of the people. A unique opportunity is now offered of developing industries hitherto swamped by foreign competition, and the nation relies upon the enterprise of its scientific men to attack the subject with promptitude and vigour. It is satisfactory to find the Government has already taken the matter up, and a Committee has been appointed to consider and advise as to the best means of obtaining for the use of British industry, sufficient supplies of chemical products, colours, and dyestuffs of kinds hitherto largely imported from a country with which we are at present at War. The committee consists of:—The Lord Chancellor (Chairman), Dr. George T. Beilby, F.R.S., Dr. J. J. Dobbie, F.R.S., Mr. David Howard, Mr. Ivan Levenstein, Prof. Raphael Meldola, D.Sc., F.R.S., Mr. Max Muspratt, Prof. W. H. Perkin, Ph.D., D.Sc., F.R.S., Mr. Milton Sharp, Sir Arthur J. Tedder, Mr. Joseph Turner, Mr. T. Tyrer, together with Mr. John Anderson, of the National Health Insurance Commission, and a representative of the Board of Trade. The secretary, Mr. F. Gossling (of the Patent Office), should be addressed at the Commercial Intelligence Branch of the Board of Trade, 73, Basinghall Street, E.C.

The Secretary of the Institute of Chemistry of Great Britain and Ireland announces that the services of qualified consulting analytical and technological Chemists are at the disposal of manufacturers, who may communicate with the Registrar at 30, Bloomsbury Square, London, W.C.

The most urgent necessity undoubtedly is the preparation of Drugs, and many great firms have shown themselves to be alive to their opportunities and to the Nation's requirements. Messrs. Burroughs, Wellcome, and Co., who for many years have manufactured several important alkaloids, such as atropine, hydrastine, &c., have already announced that they intend to continue to sell them as long as possible at the usual rates, and doubtless they will extend the manufacture as far as is practicable and necessary. The stocks of certain drugs are exceedingly low, and as far as can be foreseen it may be difficult to get additional supplies for some considerable time. Such are salicylic acid and its salts and derivatives, including aceto-salicylic acid or aspirin; it seems probable it would be worth while for manufacturing chemists to consider the question of its synthesis. All potassium salts are likely to be almost unobtainable, and also the bromides. The glycerophosphates and liquid paraffin are substances which might be made in England as well as synthetic benzoic acid and its salts. There is a decided shortage of some other drugs, but it is probable that the original sources of supply may be reopened or new sources found. In this second class are included citric and tartaric acids, ergot, formaldehyde and its derivatives, the synthesis of which in England should present no difficulties, and hexamethylene tetramine. Closely allied to the preparations of drugs is the synthesis of perfumes, the production of which in this country has seriously suffered from the restrictions placed upon the manufacture and storing of pure alcohol. The removal or modification of these restrictions would greatly lighten the difficulties under

which the manufacturers of synthetic perfumes have long laboured, and the British Government may be confidently trusted to consider the question sympathetically and to remove disabilities. A purely British Eau de Cologne is already advertised, and it is to be hoped that it will soon be followed by many other examples of scents made entirely in England. Large quantities of synthetic perfumes for soap and of synthetic flavouring substances are at present imported; the manufacture of many of them in England should present no insurmountable difficulties.

The preparation of ammonia from atmospheric nitrogen and hydrogen has been successfully performed on a large scale by the "Badische Anilin und Soda Fabrik" at Oppau; the details of the process will well repay careful study. An outline was sketched in a recent lecture by Dr. Arthur W. Crossley (*Pharmaceutical Journal and Pharmacist*, May 2, 9, and 16), in which further references will also be found. In the same lecture an account is given of the artificial hardening of fish-oil for the preparation of soap, lubricating materials, and food-stuffs. For the preparation of hydrogen for the hardening process attention may be called to the Bergius process worked in Hanover with very satisfactory results as regards purity and economy.

The case of the aniline dyes at once occurs to the mind as an industry which has been lost to England but which now may be recaptured if vigorous steps are taken by our manufacturers. The disappearances of the preparations of the Badische Anilin und Soda Fabrik, the Chemische Fabrik Griesheim-Elektron, the Actien Gesellschaft für Anilin-Fabrikation, the Chemische Fabriken vorm. Weilerter Meer, &c., should give a great impetus to the use of English made dyes; it is earnestly to be hoped that dye-makers will take the opportunity of extending their operations and enlarging their factories.

The manufacture of glass, which is at present one of the United Kingdom's largest staple imports from Germany, will be greatly encouraged by the impossibility of obtaining fresh stocks of the foreign article, and it is to be hoped that by the time genuine Jena glass, for instance, is ready to make its reappearance in the English markets it will find its place taken by British made glass of similar composition and properties. The preparation of tungsten, for lamps and for steel making, from wolfram ore is a comparatively small industry which offers great possibilities for development in England.

Continental firms have long taken a prominent part in the sale of instruments and apparatus for chemical laboratories; their goods have been widely used in this country and have acquired a deservedly high reputation. It is satisfactory, however, to note that there are firms whose productions are no less excellent, and whose works, materials, &c., are entirely British. Such, for example, are Messrs. Oertling, whose balances are well known; while the names of Hopkin and Williams, London, Boake, Roberts, and Co., London, Thos. Tyrer and Co., London, John J. Griffin and Sons, London, F. E. Becker and Co. (W. and J. George), London, Townson and Mercer, London, Baird and Tatlock, London, A. C. Cossor (Glass Apparatus), London, The Silica Syndicate, London, Fredk. Jackson and Co., Manchester, J. Woolley, Sons, and Co., Manchester, Brotherton and Co., Leeds, Reynolds and Branson, Leeds, Brady and Martin, Newcastle on Tyne, and many others will at once occur to the minds of those interested in laboratory or works equipment.

It must be remembered that the British manufacturer has now an unprecedented opportunity of obtaining a footing in certain foreign markets. For example, Denmark imports large quantities of medicinal and toilet articles, soaps, &c., and should prove a valuable customer for Great Britain. The financial situation in the country is reported to be exceptionally good, and communication by steamer is safe and regular. The firm of C. Mitchell and Co., Ltd., 1 & 2, Snow Hill, to whom the leading Danish paper *Politiken* has addressed a letter on the subject, will gladly place the services of their Export Bureau at the dis-

posal of British merchants who wish to take advantage of this chance of extending their business.

Finally, the present time offers great opportunities to agriculturalists to increase the areas devoted to the cultivation of certain classes of crops. First and foremost is the Sugar Beet, the production of which in England has been shown to be practicable and lucrative; the encouragement of its cultivation among farmers, who need to be assured of a ready and convenient market for their crops and a fair price for the roots, should lay the foundation of a thriving industry in this country. The growth of plants for the extraction of essences and perfumes is another instance of an occupation little followed in England which might with advantage be very greatly extended.

A word of warning may not be out of place. The commercial war upon Germany will require sacrifices, not comparable with those made by the men who are actually in Arms, but at the same time of considerable magnitude. It will be no easy matter for manufacturers to organise, to deal with the problems with which they will be confronted, and to overcome the great difficulties they are sure to meet. Victories will not be won at once, nor without strenuous efforts and gigantic self-sacrifices, and it may be found that very small profits, or even none at all, must be accepted with philosophy. Again, the recruits in the new army of chemists must be content to acknowledge themselves to be, comparatively speaking, untrained, and worth at first only a small remuneration. Our technical men as well as our students have much to learn, but a determined effort to make the utmost of all opportunities should help us some way along the road. True patriotism which will give its best services at the least cost will not be found wanting among scientific men, who will look hopefully to the public to replace Goods "made in Germany" by Goods made in England.

ON BOILING POINTS IN HOMOLOGOUS SERIES.

By S. SUGDE.

THE earliest relation between the boiling-points of the members of a homologous series was given by Kopp (*Ann.*, xli., 86, 169). He supposed that the boiling-point was raised 19° C. by each increment of CH_2 .

It soon became evident as more members were added to each series that the difference between the boiling-points of adjacent members decreased as the series was ascended. Several formulæ were proposed during the eighties by Mills, Hinrichs, Goldstein, and others, but as these contain three or more constants or were only valid over a short range they are not of great importance. The first formula which admitted of general application was given by Dr. James Walker in 1894 (*Journ. Chem. Soc.*, 1894, p. 193), namely,—

$$T = aMb.$$

Here T is the boiling-point measured on the absolute scale of temperature, and M the molecular weight. " a " and " b " are arbitrary constants chosen for each series.

This formula was applied to the paraffins, ethers, methyl esters, fatty acids, &c., and predicted with considerable accuracy the boiling-points of the higher members of those series. For the first few members, however, there was often a considerable difference between the observed and calculated values of the boiling-point.

In 1899 Enrico Boggio Lera (*Gazz. Chim. Ital.*, xxix., [i.], 441) proposed the formula—

$$T = R\sqrt{M} + c.$$

This formula was applied to a variety of series, paraffins, ethers, halogen derivatives, &c., and, in general, may be said to fit as well as that of Walker. It has, however, the same fault, for it is considerably in error for the first few members of several series.

In 1904 H. Ramage (*Proc. Camb. Phil. Soc.*, xii., 445) proposed the formula—

$$T = a\sqrt{M(1-2^{-n})}$$

for the paraffins only. n is the number of carbon atoms in the chain. This formula holds very accurately for the paraffins from CH_4 to $\text{C}_{17}\text{H}_{36}$. It is not, however, in its present form applicable to other series, and, indeed, in some cases (e.g., alcohols, fatty acids) no formula of this type can be applied, for $T/\sqrt{M}$ decreases as the series is ascended.

These formulæ all express the boiling-point as a function of the molecular weight. In 1905 Dr. S. Young abandoned this idea, and expressed the difference between the boiling-points of two adjacent members of a series in terms of the boiling-point of the first one. He proposed the formula (*Phil. Mag.*, [vi.], ix., 1)—

$$\Delta = \frac{1.44 \cdot 86}{T^{0.0148} \sqrt{T}}$$

Δ is the difference in boiling-point between a member of boiling-point T and the next higher member.

This formula fits the paraffins with great accuracy, and gives good results with the higher members of most series. It is, however, considerably in error for the first few members of several series.

The writer has recently proposed the formula (*CHEM. NEWS*, cvii., 135)—

$$T = a\sqrt{M} - bM,$$

which was deduced from Van der Waals' equation. This formula, though interesting from its theoretical associations, has been found on further examination to have no advantage over those of Walker or Boggio Lera. Like them it holds for the higher members of many series, but not for the lower members.

It will thus be seen that, while none of these formulæ will represent the boiling-points of the lower members of many series, there are at least four formulæ which may equally well be used to predict the boiling-points of the higher members. Nor are these the only formulæ which are valid for the higher members; the writer has found that the following two hold just as satisfactorily,—

$$T = a\sqrt{M} + b,$$

$$T = a \log M + b,$$

and doubtless others might be found if sought for.

It is evident that a formula to be satisfactory must be valid over the whole range of all series and not only for the higher members.

The following formula has been found by the writer to fulfil this condition:—

$$T = a\sqrt{M} + \frac{b}{\sqrt{M}} + \frac{a}{b} M.$$

It may be regarded as derived from the writer's earlier formula by the addition of a third term which is the quotient of the first two.

This formula may be used to predict the boiling-points of the paraffins with almost as great accuracy as that of Ramage. Unlike the latter it can be applied to other series, and has been found without exception to hold over their whole range.

The values of the boiling-points used in the following tables have been taken from the paper of Young already mentioned. All the boiling-points there given for any particular series have been used, except in the cases of the esters and ethers. These tables have been re-arranged, and certain values are omitted as there was no point in applying the formula to a series of less than four compounds.

Table I. shows how the various formulæ fit the paraffins. For this series Walker's, Boggio Lera's, and the writer's earlier formula all reduce to—

$$T = 37.38 \sqrt{M}?$$

TABLE I.—Paraffins, R.H.

R.	T (obs.) ° Abs.	Walker, &c.		Ramage.		Young.		Sugden.	
		T (calc.) ° Abs.	Diff.	T (calc.) ° Abs.	Diff.	T (calc.) ° Abs.	Diff.	T (calc.) ° Abs.	Diff.
CH ₃	108.3	149.5	+41.2	105.7	-2.6	105.8	-1.5	109.5	+1.2
C ₂ H ₅	180.0	204.9	+24.9	177.3	-2.7	177.7	-2.3	181.4	+1.4
C ₃ H ₇	228.0	247.8	+19.8	231.9	+3.9	229.8	+1.8	232.2	+4.2
C ₄ H ₉	274.0	284.8	+10.8	275.6	+1.6	272.6	-1.4	274.0	—
C ₅ H ₁₁	309.3	317.0	+7.7	312.2	+2.9	309.4	+0.1	309.2	-0.1
C ₆ H ₁₃	342.0	346.5	+4.5	343.9	+1.9	341.95	-0.05	340.9	-1.1
C ₇ H ₁₅	371.4	373.8	+2.4	372.3	+0.9	371.3	-0.1	369.5	-1.9
C ₈ H ₁₇	398.5	399.1	+0.6	398.3	-0.2	398.1	-0.4	395.9	-2.7
C ₉ H ₁₉	422.5	422.8	+0.3	422.5	—	422.8	+0.3	420.3	-2.2
C ₁₀ H ₂₁	446.0	445.4	-0.6	445.2	-0.8	445.8	-0.2	443.2	-2.8
C ₁₁ H ₂₃	467.5	466.9	-0.6	466.8	-0.7	467.4	-0.1	464.6	-2.3
C ₁₂ H ₂₅	487.5	487.3	-0.2	487.3	-0.2	487.6	+0.1	485.1	-2.4
C ₁₃ H ₂₇	507.0	507.0	—	507.0	—	506.8	-0.2	504.5	-2.5
C ₁₄ H ₂₉	525.5	526.0	+0.5	526.0	+0.5	525.0	-0.5	522.9	-2.6
C ₁₅ H ₃₁	543.5	544.2	+0.7	544.2	+0.7	542.3	-1.2	540.5	-3.0
C ₁₆ H ₃₃	560.5	561.9	+1.4	561.9	+1.4	558.8	-1.7	557.5	-3.0
C ₁₇ H ₃₅	576.0	579.0	+3.0	579.0	+3.0	574.7	-1.3	574.1	-1.9
C ₁₈ H ₃₇	590.0	595.7	+5.7	595.7	+5.7	589.9	-0.1	590.9	—
C ₁₉ H ₃₉	603.0	611.9	+8.9	611.9	+8.9	604.5	+1.5	605.4	+2.4
		Mean diff. = 1.57°		Mean diff. = 0.78°		Mean diff. = 1.98°			

It will be seen that this formula is hopelessly in error for the lower members.

Ramage's formula—

$$T = 37.38 \sqrt{M(1-2^{-n})}$$

fits well over the whole series with perhaps the exception of the last two members.

Young's formula fits exceedingly well. This is to be expected as it is a three constant formula. The constants 144.86, 0.0418, and 106.8 were chosen so as to fit the paraffins as well as possible.

The new formula—

$$T = 41.01 \sqrt{M} - \frac{205.1}{\sqrt{M}} - \frac{41.01}{205.1} M$$

holds well over the whole series. In no case does the error exceed 4.2°, while the mean difference between the observed and calculated values is less than 2°.

It has already been stated that Ramage's formula cannot be applied to other series. Tables II. and III. show how Young's formula breaks down when applied to the alcohols and fatty acids. In Young's paper the differences only are tabulated, and these are several degrees in error for the earlier members. Further, these errors are largely of the same sign, so that if the calculated differences are used to calculate the boiling-points of the whole series from that of the highest member the difference between the observed and calculated boiling-points of the lower members becomes very large.

TABLE II.—Normal Primary Alcohols, R.OH.

$$a = 34.30. \quad b = 805.5.$$

R.	T (obs.) ° Abs.	Young.		Sugden.	
		T (calc.) ° Abs.	Diff.	T (calc.) ° Abs.	Diff.
CH ₃	337.7	286.0	-51.7	337.8	+0.1
C ₂ H ₅	351.3	315.8	-35.5	353.6	+2.3
C ₃ H ₇	370.2	344.3	-25.9	372.3	+2.1
C ₄ H ₉	389.9	371.2	-18.7	391.9	+2.0
C ₅ H ₁₁	411.0	396.6	-14.4	411.3	+0.3
C ₆ H ₁₃	431.0	420.4	-10.6	430.5	-0.5
C ₇ H ₁₅	449.0	442.9	-6.1	449.1	+0.1
C ₈ H ₁₇	464.0	464.3	+0.3	467.2	+3.2
C ₉ H ₁₉	486.5	484.8	-1.7	485.0	-1.5
C ₁₀ H ₂₁	504.0	504.0	—	501.9	-2.1
		Mean diff. = 1.42°			

TABLE III.—Fatty Acids, R.CO OH.

$$a = 35.93. \quad b = 881.0.$$

R.	T (obs.) ° Abs.	Young.		Sugden.	
		T (calc.) ° Abs.	Diff.	T (calc.) ° Abs.	Diff.
H	373.6	349.8	-23.8	375.5	+1.9
CH ₃	391.1	376.4	-14.7	391.5	+3.4
C ₂ H ₅	413.7	401.7	-12.0	414.5	+0.8
C ₃ H ₇	435.3	425.3	-10.0	434.6	-0.7
C ₄ H ₉	458.0	447.4	-10.6	454.3	-3.7
C ₅ H ₁₁	477.5	468.2	-9.3	473.5	-4.0
C ₆ H ₁₃	496.5	487.95	-8.55	492.3	-4.2
C ₇ H ₁₅	509.5	506.7	-2.8	510.5	+1.0
C ₈ H ₁₇	526.5	524.75	-1.75	528.1	+1.6
C ₉ H ₁₉	542.0	542.0	—	544.6	+2.6
		Mean diff. (°C) = 2.39			

Young's formula breaks down in a similar manner when applied to several other series, e.g., aldehydes, esters, alkyl cyanides. With the new formula, however, the writer has not found one instance in which the difference between the observed and calculated values exceeds 6.3°, while, in general, the average error for a series is less than 2°.

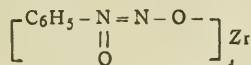
(To be continued).

THE SEPARATION OF ZIRCONIUM FROM IRON AND ALUMINIUM WITH THE AID OF THE AMMONIUM SALT OF NITROSOPHENYLHYDROXYLAMINE ("CUPFERRON").

By WILLIAM M. THORNTON, jun., and E. M. HAYDEN, jun.

In connection with a study of potassium ferrocyanide, Schröder (*Zeit. Anorg. Chem.*, 1911, lxxii., 89) has stated that both titanium and zirconium could be quantitatively precipitated by the "cupferron" reagent from their acidified solutions, and that experiments were in progress for estimating these two elements. Schröder gave no experimental data, and, as far as the authors of this paper can ascertain, has not published further upon the subject. Bellucci and Grassi (*Gazz. Chim. Italiana*, 1913, Part I., xliii., 570) have shown the "cupferron" reagent to be a quantitative precipitant for titanium, and that a clean separation of titanium from aluminium could be brought

about in solutions notably acid with either sulphuric or hydrochloric acid. Following the work of Bellucci and Grassi, one of us (*Am. Journ. Sci.*, 1914, xxxvii, 173) has pointed out that, after throwing down the iron as ferrous sulphide from a solution containing sufficient ammonium tartrate to hold up titanium, and after acidifying the iron free filtrate, the titanium can be quantitatively precipitated by the "cupferron" reagent notwithstanding the presence of tartaric acid, and, further, that if the above-mentioned filtrate be strongly acidified with sulphuric acid and contain also a sufficient quantity of tartaric acid, titanium can be quantitatively separated from both aluminium and phosphoric acid in one operation (*Am. Journ. Sci.*, 1914, xxxvii, 407). On account of the great similarity in chemical nature between titanium and zirconium it appeared probable that in a similar way zirconium could be parted from the three substances mentioned above. Experiments with a view to accomplishing these separations were very successful as far as iron and aluminium were concerned. In the case of phosphoric acid, however, it was found that the zirconium derivative of nitroso phenylhydroxylamine—



(Assuming a formula analogous to the one proposed by Bellucci and Grassi for the titanate derivative).

even when the former was present with the zirconium in relatively small quantities, carried down very appreciable masses of phosphoric acid; although the test solution contained 40 cc. of sulphuric acid (1:1) and 5 grms. of tartaric acid in a total volume of 400 cc.

On account of the great difficulty in handling these two substances when together in solution the authors decided to abandon the attempt to separate them in aqueous solution, but to recommend instead that, in the analysis of phosphatic materials containing zirconium, the phosphoric acid be separated at the beginning of the analysis by fusion with sodium carbonate and a little sodium nitrate, and leaching with water, whereupon sodium phosphate dissolves, leaving the residual sodium zirconate which is soluble in sulphuric acid (see Hillebrand, *Bull. U.S. Geological Survey*, 1910, No. 422, p. 139).

Two solutions of zirconium sulphate were used in these experiments. The first was prepared by dissolving Merck's zirconium sulphate in dilute sulphuric acid, filtering, and making up to definite volume. Four experiments were made with the object of setting the standard of this solution. In experiments (a) and (b) the zirconium was thrown down in the hot solution by re-distilled ammonium hydroxide—the precipitation being performed in a platinum basin. In experiments (c) and (d) the zirconium was precipitated by the "cupferron" reagent from a volume of 400 cc. containing 20 cc. of sulphuric acid (made by diluting acid of specific gravity = 1.84 with an equal volume of water). The following results were obtained:—

Zirconium sulphate solution.	Zirconium oxide.
(a) 25 cc. = 25.9545 grms.	0.1088 grm. 0.4157 per cent
(b) 25 cc. = 25.9415 grms.	0.1089 grm. 0.4198 per cent
(c) 25 cc. = 25.978 grms.	0.1091 grm. 0.4200 per cent
(d) 25 cc. = 25.975 grms.	0.1089 grm. 0.4192 per cent

Since the values obtained in (b) and (c) by two different methods agree so closely, (c) was arbitrarily taken as correct. The second solution was prepared by acting on twice crystallised potassium fluozirconate with sulphuric acid (1:1), warming gently until all hydrofluoric acid had been displaced, pouring into cold water, and making up to definite volume. This solution was standardised by precipitation with the "cupferron" reagent, which had already been shown to agree well with results obtained by the reliable ammonium hydroxide precipitation. Duplicate determinations gave the following results:—

Zirconium sulphate solution.	Zirconium oxide.
(a) 25 cc. = 26.550 grms.	0.1101 grm. 0.4147 per cent
(b) 25 cc. = 26.559 grms.	0.1099 grm. 0.4138 per cent

The mean of these two values was taken as correct.

The first series of experiments was performed with the object of ascertaining satisfactory conditions for the separation of zirconium from aluminium. Known quantities of zirconium and aluminium were taken by weighing off portions of the standardised zirconium solution and dry re-crystallised ammonium aluminium sulphate respectively. The solution was made neutral to methyl-orange with ammonium hydroxide, which had been re-distilled and kept in bottles of Jena glass. Measured volumes of sulphuric acid (1:1) were then added, and the solution made up to 400 cc. About 20 cc. of a 6 per cent "cupferron" solution was added gradually with constant stirring. Thereupon the zirconium came down as a very bulky and flocculent white precipitate. Without much delay the precipitate was filtered on paper with the aid of gentle suction, and washed thoroughly with hydrochloric acid (made by diluting 100 cc. of acid of specific gravity = 1.20 to 1 litre). The precipitate was placed in a tared platinum crucible, dried at 110°C., and carefully ignited to zirconium oxide. Table I. contains the results of four experiments.

TABLE I.—The Separation of Zirconium from Aluminium.

No.	ZrO ₂ taken. Grm.	Al ₂ O ₃ taken. Grm.	ZrO found. Grm.	Error. Grm.	H ₂ SO ₄ (1:1). Cc.	Volume of soln. Cc.
1.	0.1091	0.1127	0.1090	-0.0001	40	400
2.	0.1088	0.1127	0.1090	+0.0002	40	400
3.	0.1086	0.1127	0.1090	+0.0004	60	400
4.	0.1091	0.1127	0.1094	+0.0003	60	400

In the second series of experiments zirconium was separated from iron. Known quantities of iron were introduced by weighing off portions of Kahlbaum's ferrous ammonium sulphate. Since the technique is the same for the separation of zirconium from iron only as for the separation of zirconium from both iron and aluminium, the procedure will be described below for the more general case. Table II. embodies the results of two experiments.

TABLE II.—The Separation of Zirconium from Iron.

No.	ZrO ₂ taken. Grm.	Fe ₂ O ₃ taken. Grm.	ZrO ₂ found. Grm.	Error. Grm.	Tartaric acid. (1:1). Grm.	H ₂ SO ₄ . Cc.
5.	0.1088	0.1018	0.1091	+0.0003	2	40
6.	0.1090	0.1018	0.1093	+0.0003	2	40

In the third series of experiments known mixtures of iron, aluminium, and zirconium were analysed. The iron and aluminium were introduced into the solution by weighing dry portions of ferrous ammonium sulphate and ammonium aluminium sulphate, just as was done in the two series above. In Table III. are put forth the results of four experiments.

TABLE III.—The Separation of Zirconium from Iron and Aluminium.

No.	ZrO ₂ taken. Grm.	Fe ₂ O ₃ taken. Grm.	Al ₂ O ₃ taken. Grm.	ZrO ₂ found. Grm.	Error. Grm.	Tar-taric acid. (1:1). Grm.	H ₂ SO ₄ soln. Cc.	Vol. of solution. tion.
7.	0.1087	0.1018	0.05635	0.1086	-0.0001	2	40	400
8.	0.1089	0.1018	0.05635	0.1088	-0.0001	2	40	400
9.	0.1101	0.2036	0.1127	0.1110	+0.0009	2	40	400
10.	0.1100	0.2036	0.1127	0.1103	+0.0003	2	40	400

The technique of the analysis is here connectedly given. Tartaric acid is added to the solution in amount equal to five times the aggregate weight of the three bases to be held by it in solution. It is desirable that the initial volume of the test solution should not much exceed 100 cc. To facilitate reduction of the iron the solution is made neutral to litmus-paper with ammonium hydroxide and

then acid again with 2 cc. of sulphuric acid (1 : 1). Hydrogen sulphide is then passed in until the iron has all been reduced to the ferrous state. The solution is now made slightly ammoniacal and more hydrogen sulphide introduced till the iron has been completely thrown out as ferrous sulphide, leaving the solution, however, alkaline to test-paper. The ferrous sulphide is thrown on a filter and washed ten times with very dilute colourless ammonium sulphide. The filtrate is acidified with 40 cc. to 60 cc. of sulphuric acid (1 : 1) and the hydrogen sulphide thus liberated boiled out. The solution is then cooled (best by iced water), the volume made to 400 cc., and the "cupferron" reagent added gradually in the cold with constant stirring. Without delay the filtration is proceeded with, using a paper filter and mild suction. The filtrate should be tested as to completeness of precipitation by adding thereto a few drops of the reagent. A white turbidity will appear immediately if the solution still contain zirconium—otherwise a small white precipitate of nitrosophenylhydroxylamine which disappears on standing. After a little experience the analyst will have no difficulty in distinguishing these two precipitates, which are very different in appearance. The precipitate is washed at least twenty times with hydrochloric acid (100 cc. of acid of sp. gr. = 1.20 diluted to 1 litre), agitating the filter contents as much as possible, and not allowing the washing fluid to run through too fast to accomplish much solvent work. After having been sucked free from drainage liquid at the pump, the precipitate along with the filter is placed in a tared platinum crucible and dried at 110° C. If it be desired to save time, the ignition can be started with the precipitate moist exercising great care, however, to avoid loss by spattering. With the lid not quite covering the crucible, the volatile matter is cautiously smoked off, the residual carbon burned away, the Meker burner applied for one half-hour, and the zirconium oxide weighed. The ignition should be repeated, of course, until a constant weight is obtained.

In order to determine to what extent the zirconium derivative of nitrosophenylhydroxylamine includes fixed alkalis when salts of the latter are present in the solution, zirconium determinations were made in the presence of a large excess of potassium sulphate. The mode of experimentation was the same as that employed in the case of the separation of zirconium from aluminium. Table IV. shows the results of two experiments.

TABLE IV.—The Separation of Zirconium from Potassium.

No.	ZrO ₂ taken. Gm.	K ₂ O taken. Gm.	ZrO ₂ found. Gm.	Error. Gm.	H ₂ SO ₄ (1 : 1). Volume of soln. Cc.
11.	0.1088	2.7027	0.1097	+0.0009	40 400
12.	0.1089	2.7027	0.1096	+0.0007	40 400

It will be observed that the gain of weight undergone by the zirconium is not very large, and when one considers that the amount of potassium present (calculated as oxide) is nearly twenty-five times as great as the zirconium (also reckoned as oxide), the tendency of the precipitate to carry down alkalis need not be regarded as serious.

It remains now only to call attention to the chief points of merit possessed by this method of analysis. The precipitation of zirconium by the "cupferron" reagent is quantitative. From solutions strongly acidified with sulphuric acid, a clean separation of zirconium from aluminium can be effected. Tartaric acid does not interfere with the precipitation, so that the acidified filtrate from the ferrous sulphide is in fit condition for the separation of zirconium from aluminium—a fact which obviates the necessity for oxidising the organic oxy-acid. The precipitate comes down immediately in flocculent and readily filterable condition, is little prone to include alkalis, and after drying can be converted into zirconium oxide of a high degree of purity. The manipulation is extremely simple and the sources of error are few.—*American Journal of Science*, 1914, xxxviii., p. 137.

A METHOD FOR THE DETERMINATION OF MAGNESIUM IN CALCIUM SALTS.*

By J. C. HOSTETTER.

IN the course of the preparation of some calcium silicates for thermal study, certain samples of calcium carbonate were tested to determine their suitability as sources of lime. Analyses of these samples showed that, of the non-volatile impurities determined by the makers, the amounts reported by them were substantially correct for all elements except magnesium (with the possible exception of sodium, for which the makers' "trace" was found to be 0.02 per cent Na₂O). This element was found to be present to the extent of several tenths of a per cent as oxide, even though the salts analysed were of the very highest grades obtainable, and the makers' analyses had shown but a "trace," or, at most, 0.005 per cent MgO. A discrepancy of this large order could hardly be passed over without investigation, even though the problem thus presented was but a mere side issue. The writer's results on these samples had been obtained by the calcium sulphate separation, but, since the laboratory manipulation of this method was too involved for routine testing when large samples were taken, a method was developed by means of which very small amounts of magnesium could be determined in the presence of much calcium, and which involved only the simplest laboratory manipulation. After this method had been developed, a number of calcium salts, from both domestic and foreign makers, were tested to determine their suitability for the particular problem in hand, but the surprisingly large quantities of magnesium found to be present were the source of much disappointment. In a few cases, the makers' results were of the same order of magnitude as those obtained by the new method, but usually the magnesia actually present was from fifty to even several hundred times greater than that reported by the maker. The probable source of the observed differences will appear in what follows.

Most of the methods employed for the determination of magnesium in the presence of calcium involve a removal of the latter by precipitation and a subsequent estimation of the former in the filtrate. In general, when testing for minute amounts of impurity, the procedure of first removing the main element by precipitation should never be followed. In some cases it can be justified, but these are rare and they can be determined only by direct test; in the greater number of cases the precipitating salt carries with it a large portion, if not all, of the impurity, and hence the amount of the latter subsequently found is much less than that actually present. Many methods of separation which are excellent when applied to tests in which the elements to be separated are present in nearly equal amounts fail utterly when the one element is present to the extent of a thousand times that of the other. This latter condition is the main one involved in the problem here studied, and failure to recognise this is the general reason why chemical manufacturers have often failed to find out all of the magnesium present in their calcium salts. The specific manner in which loss of magnesium may occur in the ordinary methods of separating calcium and magnesium will appear in the discussion which follows.

Removal of Calcium as Oxalate.—The extensive investigation of Richards, McClaffrey, and Bisbee (*Zeit. Anorg. Chem.*, 1901, xxviii., 71; *Proc. Am. Acad. Arts Sci.*, 1901, xxxvi., 375) on the occlusion of magnesium by calcium oxalate has shown that when the latter is precipitated in the presence of magnesium under certain conditions, the resulting calcium oxide may carry as much as 16.4 per cent MgO; under the usual conditions for this precipitation, the occlusion may still amount to about 1 per cent. Only with careful attention to the details of the

* From the *Journal of Industrial and Engineering Chemistry*, vi., No. 5.

method proposed by them can a satisfactory separation of calcium from magnesium be made with one precipitation of the calcium oxalate.

Ordinarily, in exact analysis, two precipitations of the oxalate are deemed necessary for a good separation, and when the elements are present in nearly the same amount, this is justified. When large amounts of calcium and mere traces of magnesium are present, however, two precipitations, or even more, will not separate these two elements quantitatively.

In view of the convincing character of the work cited above, it is indeed surprising that texts on the subject of reagent testing should continue to prescribe the determination of magnesium in a solution from which calcium has been removed as oxalate, when calcium salts are to be tested for this impurity. As carried out by Krauch ("Testing of Chemical Reagents," 3rd ed., p. 60), and by Krauch-Merck ("Chemical Reagents, their Purity and Tests," p. 80), the calcium of 1 grm. of the salt is precipitated as oxalate and the salt is considered satisfactory if sodium phosphate solution gives no precipitate in the filtrate on standing twelve hours.

Removal of Calcium as Sulphate.—This separation, as outlined by Classen ("Ausgewählte Methoden d. Anal. Chem," Erster Band, p. 835), is comparatively free from the errors inherent in the oxalate and carbonate precipitations. That calcium sulphate precipitated in the presence of magnesium carries a negligible amount of magnesia (occluded or otherwise) is shown by the following experiment:—The calcium of 5 grms. of a pure calcium chloride in alcoholic solution was precipitated with sulphuric acid in the presence of 250 mg. MgO (added as chloride). The calcium sulphate was filtered off and washed with 50 per cent alcohol in the prescribed manner. After drying, the magnesia was determined in this calcium sulphate by the new method to be described shortly, and found to be but 0.005 per cent. (In this connection, it is interesting to note that magnesium is occluded less by precipitating barium sulphate than any other metal which has been studied. Allen and Johnston, *Journ. Am. Chem. Soc.*, 1910, xxxii., 612; Johnston and Adams, *Ibid.*, 1911, xxxiii., 832). In many cases the magnesia thus lost would be insignificant, but this loss could not be tolerated in the analysis of the purest calcium salts.

Though this method of removing calcium is fairly satisfactory in regard to the amount of magnesia occluded, it has the disadvantage that when large amounts of calcium are to be removed, the laboratory manipulation becomes difficult. This is due to the bulky nature of the precipitated calcium sulphate, the many tedious washings of the precipitate which are required, and the evaporation to dryness of several litres of alcoholic solution. Accordingly, we have discontinued the use of this method except as an occasional check.

The discrepancy observed between the makers' magnesia determinations and the writer's results by the calcium sulphate separation can be completely accounted for on the reasonable assumption that the makers follow the oxalate separation as given in the standard tests on reagent testing. Direct evidence on this point is generally lacking, but in the case of one maker at least, the labels specify that the salt has been tested according to Krauch (Merck and Company, "Blue Label Reagents"). In the absence of specific information on this subject from the other makers (requests for information on this point were ignored by an American maker), we can only assume that their results were also secured with the calcium oxalate separation on a comparative small sample.

Removal of Calcium as Carbonate.—It is well known that the separation of calcium as carbonate involves the same source of error as the oxalate separation—some magnesium is occluded by the calcium carbonate. The extent of this occlusion is indicated by the amount of MgO remaining in calcium carbonates of the highest grade—about 0.08 per cent (the average of the MgO contents of the calcium carbonates given in Table II.).

The Method of Hildebrand and Harned.—This excellent method for the determination of magnesium in the presence of calcium (and other metals) is a precipitation of the magnesium as hydroxide, the precipitant being sodium hydroxide and the changes in hydrogen in concentration being followed by means of the hydrogen electrode (*Orig. Com. 8th Inter. Cong. Appl. Chem.*, 1, 217; *Journ. Am. Chem. Soc.*, 1913, xxxv., 867). Since the uncertainty in the end-point, as given by them, may amount to as much as 4 mg. MgO, it is evident that this method could be used in connection with the present problem only in the case of highly impure calcium salts.

The Proposed Method.

The essential feature of the method that follows is the concentrating of the magnesium from a large sample of the salt being tested into a precipitate containing but a small proportion of the calcium. After this has been accomplished the ordinary methods may be used to separate these elements with satisfactory results, since the ratio CaO:MgO is no longer 1000 or 10,000:1, but has been reduced to 10 or 100:1. This concentrating is effected by precipitating the magnesium as hydroxide by adding either calcium oxide (made, in many cases, by ignition of the salt itself) or a solution of sodium hydroxide in slight excess over that necessary to precipitate the magnesium. (Compare the method of analysis of high-grade zinc by F. Mylius and O. Fromm (*Zeit. Anorg. Chem.*, 1895, ix., 149), in which they concentrate the impurities into a sulphide precipitate containing very little zinc). The details of the method follow.

Ten grms. of calcium salt are brought into solution in water, and the volume made up to 100 cc. If acid is used to bring the salt into solution, the excess is neutralised with sodium hydroxide, after the expulsion of CO₂, SO₂, &c., by boiling. The calcium oxide made from 0.3 to 0.5 grm. calcium carbonate by ignition is now added and the solution heated to boiling; the precipitate is filtered off but not washed. (These need be weighed only to 5 per cent; the amount to be used depends on the MgO content of the salt—*cf. postea*). The precipitate is dissolved in dilute hydrochloric acid and the calcium removed by two precipitations with ammonium oxalate. The filtrates from these two precipitates are combined and the magnesium in this combined filtrate is determined by precipitation as ammonium magnesium phosphate with microcosmic salt. This precipitation is easily brought about by shaking in a stoppered flask. After standing several hours the precipitate is filtered off, washed free from phosphoric acid with 10 per cent ammonia, and finally ignited to magnesium pyrophosphate, which is weighed.

Factors Affecting this Method.

1. Solubility of Calcium Hydroxide in Solutions of Calcium Chloride.—A knowledge of the solubility of calcium hydroxide in 10 per cent calcium chloride solution is necessary in order to determine the amount of calcium oxide to be added to the chloride solution. The calcium oxide must be added in amount somewhat more than sufficient to saturate the solution with respect to calcium hydroxide and to precipitate the magnesium as hydroxide. From the data of Zahorsky and of Lunge (as given by Seidell, "Solubilities of Inorganic and Organic Substances," p. 91, 1st ed.) we find that 100 cc. of a 10 per cent calcium chloride solution will dissolve 0.13–0.14 grm. calcium oxide at 80° to 100°. One grm. of calcium carbonate yields 0.560 grm. calcium oxide, and for the precipitation of 1 grm. magnesia there is required 1.392 grm. calcium oxide. These figures, together with the solubility, show that the calcium oxide made from 0.5 grm. calcium carbonate will saturate the solution, and is in slight excess over that required to precipitate 0.100 grm. MgO—equal to 1 per cent on a 10 grm. sample. Similarly, calculation shows that 0.4 grm. calcium carbonate will precipitate 0.6 per cent MgO in a 10 grm. sample, and 0.3 grm. calcium carbonate will precipitate 0.2 per

TABLE II.—Magnesia found in High-grade Calcium Salts from different Makers.

Salt.	Maker.	Description.	Lot No.	Magnesium oxide (per cent).		
				Maker's analysis.	Hydroxide concentration method.	MgO calculated as per cent of CaO.
Acetate ..	B. and A.	"C.P."		No anal.	2.027	0.076
	E. and A.	"Tested purity."	B 83	—0.001	0.041	0.11
	J. T. B.	"C.P." Analysed.	51313	—0.001	0.001	0.002
	B. and A.	"C.P." Analysed.		Trace	0.090	0.16
	B. and A.	"C.P." Analysed.		No anal.	0.25	0.44
	B. and A.	"Special."		No anal.	—0.001	0.00
	J. T. B.	"C.P." Analysed.	8212	0.001	0.039	0.068
	J. T. B.	"C.P." Special.		—0.001	0.048	0.085
	J. T. B.	"C.P." Analysed.	101212	0.001	0.056	0.10
	J. T. B.	"C.P." Analysed.	5513	0.005	0.027	0.048
Carbonate ..	J. T. B.	"C.P." Analysed.	101613	0.005	0.10	0.17
	E. and A.	"Tested purity."	B 33	0.005	0.27	0.48
	Kb.	"Zur Anal. m. Garantieschein."	4782	0.000	0.062	0.11
	M.	"Blue label reagent."	10853	Free	—0.001	0.00
	M.	"Blue label reagent."	12303	Free	0.000	0.000
		Iceland spar.			0.047	0.084
	B. and A.	"C.P." Fused granular.		Trace	0.058	0.11
	J. T. B.	"C.P." Analysed cryst.	103012	0.001	0.009	0.023
	J. T. B.	"C.P." Analysed cryst. (diff. bottle)	103012	0.001	0.066	0.015
	J. T. B.	"C.P." Analysed anhyd.	10912	0.001	0.042	0.083
Chloride ..	J. T. B.	"C.P." Analysed anhyd.	11612	0.001	0.15	0.29
	J. T. B.	"C.P." Analysed anhyd. (12-mesh)	121812	0.005	1.44	2.85
	J. T. B.	"C.P." Analysed anhyd.	112112	0.01	0.23	0.45
	J. T. B.	"C.P." Analysed cryst.	122211	0.002	0.065	0.17
	M.	"Blue label reagent," fused.	10353	Not det.	0.023	0.045
	J. T. B.	"C.P." Analysed.	61812	None	0.005	0.038
Formate ..	J. T. B.	"Technically pure."	32213	0.05	0.87	1.14
Hydroxide ..	M.	"Blue label reagent."	1472	Not det.	0.68	0.89
	J. T. B.	"C.P." Analysed cryst.	101712	0.001	0.14	0.59
Nitrate ..	E. and A.	"Tested purity."	B 13	None	0.31	1.31
Oxalate ..	Kb.	White label.	L 2801	No anal.	0.041	0.084
Oxide ..	J. T. B.	From marble.	32413	0.51	1.18	1.18
	Kb.	"Zur Anal. m. Garantieschein."		Not det.	0.77	0.77
Sulphate ..	M.	"Blue label reagent."	11513	Free	0.007	0.021
Sulphite ..	E. and A.	"Tested purity," cryst.	B 83	0.05	0.36	1.00

Abbreviations.

B. and A.—Baker and Adamson Chemical Company, Easton, Pa.
J. T. B.—J. T. Baker Chemical Company, Pittsburg, N.J.
E. and A.—Eimer and Amend, New York, N.Y.
Kb.—C. A. F. Kahlbaum, Berlin.

M.—Merck and Company, New York, N.Y.
No anal.—No analysis on label.
Not det.—Analysis on label, but MgO not determined.
Free.—Free from MgO as tested by Krauch's method.
—0.001.—Less than 0.001 per cent MgO.

cent MgO. It is obviously of great advantage to use the smallest possible amount of calcium oxide in this precipitation, and, for most salts, the oxide from 0.3 grm. calcium carbonate suffices.

II. Solubility of Magnesium Hydroxide in Calcium Chloride Solutions Saturated with Calcium Hydroxide.

No information on this subject has been found in the literature. We have qualitatively estimated the effect of this solubility on the method, and have concluded that it is nearly negligible. The tests were made by determining the magnesia in 10 grm. portions of a certain sample of calcium chloride, keeping all conditions constant except the volume of the solution in which the magnesium hydroxide was precipitated. This volume was varied from 25 cc. to 200 cc. The results showed that the change of solubility with increasing dilution is, fortunately, small. We have accordingly chosen the 10 per cent dilution as a convenient volume in which to work, and one in which the error due to solubility is probably not over 0.2 mgrm. MgO for 100 cc.

This crude method of investigating the solubility of magnesium hydroxide in solutions of calcium chloride saturated with calcium hydroxide was made necessary on account of the difficulty of obtaining calcium salts free from magnesium and magnesium salts free from calcium.

It was thought to be beyond the scope of this paper to prepare suitable materials and actually determine this solubility. One experiment on the solubility of magnesium hydroxide in calcium hydroxide solution saturated at 90° was made by determining the magnesium in the liquid phase after having removed the calcium as sulphate. The magnesia in 100 cc. of this solution is probably less than 0.1 mgrm., since the precipitate of ammonium magnesium phosphate was too small to be filtered off and weighed.

III. Use of Sodium Hydroxide as the Precipitant.—It is obvious that a known amount of sodium hydroxide may be used to precipitate the magnesium and a slight excess of calcium hydroxide. Where acid has been used to bring a calcium salt into solution, the excess acid is carefully neutralised, using methyl orange as indicator, and then an amount of sodium hydroxide solution is added, sufficient to precipitate the magnesium and a slight amount of calcium hydroxide. From this point on, the procedure is exactly as outlined under the calcium oxide precipitation.

In the work of Hildebrand and Harned quoted above it is mentioned that the change in hydrogen ion concentration when the magnesium hydroxide has all been precipitated and the calcium hydroxide is beginning to precipitate, is too gradual to be shown by an indicator.

Nevertheless, it was hoped that an indicator could be found by the change of which an indication would be given, when sodium hydroxide was used, that the hydrogen ion concentration corresponding to a precipitation of some small amount of calcium hydroxide had been reached. Several indicators of appropriate turning point (10^{-12} to 10^{-13}) were tested, but the results obtained were erratic. This was partly due to the fact that there are comparatively few indicators giving sharp colour changes in this region of hydrogen ion concentration, and very probably also that there was a large "salt effect" due to the highly concentrated calcium chloride solution.

The precision obtainable by the hydroxide concentration method, and the agreement between it and the sulphate separation, are shown in Table I. These analyses on carefully mixed samples of calcium carbonate were run side by side. On still another sample of calcium carbonate, the writer obtained 0.09 per cent MgO, using the new method with but one precipitation of the oxalate, while Dr. H. S. Washington, of the Geophysical laboratory, found 0.12 per cent MgO, using the same method but making two careful precipitations of the calcium oxalate. The difference is about what would be occluded by the first precipitate of calcium oxalate.

TABLE I.—Percentages of Magnesia.

Sample.	By hydroxide concentration.	By sulphate separation.
A	0.091	0.074
	0.091	0.090
	0.089	—
	0.090	—
B	0.25	0.25

Notes on the Method.—Since the effect of the salts of other acids on the solubility of magnesium hydroxide in calcium chloride solutions saturated with calcium hydroxide has not been determined, it is advisable to ignite such calcium salts as the nitrate, acetate, formate, and oxalate to oxide, and then dissolve all but a portion equivalent to the 0.3–0.5 grm. of CaCO_3 , in dilute hydrochloric acid, using methyl-orange as indicator. The reserved portion of oxide is added as the precipitant, thus removing the possibility of introducing magnesium as an impurity in the calcium oxide made from calcium carbonate, or in the sodium hydroxide. The carbonate, hydroxide, oxide, sulphite, and sulphate should be dissolved directly in hydrochloric acid.

Traces of calcium as tricalcium phosphate are frequently present to the extent of some 0.3–0.5 mgrm. in the magnesium pyrophosphate, and may be corrected for by dissolving the ignited (and weighed) precipitate in a little dilute sulphuric acid, adding alcohol, and allowing to stand over night. The calcium sulphate is filtered off and weighed as such; or it may be converted into oxalate and weighed as oxide.

It is obvious that there is practically no limit to the size of the sample from which the magnesium can be concentrated by this method, thus allowing almost any desired precision in the amount of magnesium weighed. A 10 grm. sample will permit of 0.001 per cent MgO being approximately determined. We have used at times samples of 20 and even 100 grms. with this method.

The oxalate separation has been used after the hydroxide concentration in order to combine in one precipitation the removal of calcium and also the slight amounts of iron and aluminium which may be present. While the sulphate separation is undoubtedly the better, it requires an evaporation and a separate precipitation for the other impurities.

Results obtained by the Hydroxide Concentration Method.—In Table II. are given the results on the magnesia content of all the samples tested by the new method. As will be seen by an inspection of the table, these samples are from all of the more widely known makers of analysed chemicals. In presenting these results there is absolutely

no discrimination, and we think that a comparison of the makers' determinations as given in the table will support our statement that all the makers are equally at fault in this particular. We publish these data not as a criticism of the makers, but solely to present the facts in the case as we find them, with the hope that their publication may help to bring about the more complete elimination of magnesia from calcium salts, and hence to help raise the standard of analysed chemicals. We think that in presenting the matter in this way, it is fairest both to the maker and to the user. With this presentation of the subject, our direct interest must end, since, as stated at the beginning, the problem was but a mere side issue, and further testing of calcium salts on our part has been rendered unnecessary, as we have secured by purchase enough of the purest of the lots tested to last us several years.

For many purposes where the highest grade calcium salts are used, the presence of much magnesia may be regarded as a matter of indifference. The two elements are chemically very similar; the reactions of one may not interfere with those of the other. Whether the presence of magnesium in calcium salts is objectionable for certain purposes or not is, however, aside from the main issue. The point to be emphasised is that the makers analyses should represent exactly the amounts of impurities present. Only in this manner can the makers' analyses be of any real service to the user of analysed chemicals.

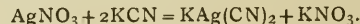
A NEW METHOD FOR THE DETERMINATION OF HYDROCYANIC ACID AND THE ALKALI CYANIDES.

By G. E. F. LUNDELL and J. A. BRIDGMAN.

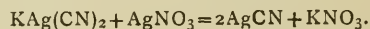
ONE gravimetric and five different volumetric methods have already been proposed for the above named determination. The authors' excuse for bringing out still another method is that the proposed method is superior to the older methods in several important respects. For the sake of comparison, the following very brief reviews of the existing methods are given.

In the gravimetric method the cyanide is precipitated in a weak nitric acid solution as silver cyanide, which is either dried at 100°C . and weighed as such, or ignited and weighed as silver. This method is open to at least three objections:—(1) It requires too much time; (2) the results obtained are invariably too high, since chlorides and sulphocyanates, which are commonly present in commercial cyanides, are also precipitated by silver nitrate in a weak nitric acid solution; (3) when a large number of determinations are made the method is too expensive.

Liebig's Method (*Ann.*, 1851, lxxvii., 102) depends on the fact that soluble potassium silver cyanide is first formed when an aqueous solution of a cyanide is treated with a silver nitrate solution,—



When silver nitrate in excess of that required for the above reaction has been added, the potassium silver cyanide is decomposed with the separation of insoluble silver cyanide which renders the solution turbid.



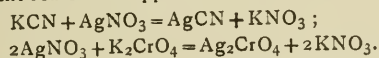
Therefore standard silver nitrate solution is added to the prepared cyanide solution until a permanent opalescence is obtained. The objections to this method are at least three in number:—(1) The results obtained are usually too high, since alkali carbonates, sulphocyanates, and ferrocyanides delay the end-point; (2) the titration requires a perfectly clear solution; (3) when a large number of determinations are made the method is costly, each titration requiring 50 cc. 0.1-N AgNO_3 solution, costing about two cents.

Hannay's Method (*Journ. Chem. Soc.*, 1878, xxxiii., 245).—An ammoniacal solution of a cyanide when treated with mercuric chloride will give no precipitate until the completion of the reaction expressed by the equation $4\text{KCN} + \text{HgCl}_2 = \text{K}_2\text{Hg}(\text{CN})_4 + 2\text{KCl}$. When the potassium cyanide has been used up in accordance with the above reaction, further addition of mercuric chloride causes a precipitation of mercurammonium chloride, which imparts an opalescence to the solution, $\text{HgCl}_2 + 2\text{NH}_4\text{OH} = \text{NH}_2\text{HgCl} + \text{NH}_4\text{Cl} + 2\text{H}_2\text{O}$. Hence a standard mercuric chloride solution is added to the prepared cyanide solution until a permanent opalescence is produced. This method gives good results in most cases. Some objections are:—(1) The difficulty experienced in correctly standardising the mercuric chloride solution; (2) the titration requires a perfectly clear solution; (3) ferrocyanides delay the end-point, thereby causing high values on samples containing this impurity.

Fordos and Gelis's Method (*Journ. Prakt. Chem.*, 1899, lix., 255) is based on the behaviour of iodine towards potassium cyanide, $\text{KCN} + \text{I}_2 = \text{KI} + \text{CNI}$. A standard iodine solution is added to the prepared cyanide solution until a permanent yellowish tinge is obtained. The results obtained by this method are not accurate and the interferences are numerous.

Andrew's Method (*CHEM. NEWS.*, 1903, lxxxviii., 239).—The diluted solution of hydrocyanic acid or a simple cyanide is made just alkaline to parantitrophenol. At this point all of the original hydrocyanic acid or cyanide is present as hydrocyanic acid, since this acid is without effect on the indicator. The solution is then treated with an excess of mercuric chloride, $2\text{HCN} + \text{HgCl}_2 = \text{Hg}(\text{CN})_2 + 2\text{HCl}$. Upon the completion of the reaction, the liberated hydrochloric acid is titrated with 0.1-N sodium hydroxide. This method works well with pure cyanides, but is not accurate when used on commercial material. Then, too, the method takes too much time.

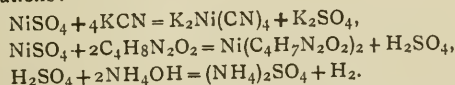
Vielhaber's Method (*Arch. Pharm.*, [iii.], xiii., 408).—In this method the cyanide solution is made alkaline by the addition of magnesium hydroxide suspended in water. After the addition of a few drops of chromate indicator, the solution is titrated with 0.1-N silver nitrate until a permanent red colour appears.



This method is not accurate. Besides the inherent error of the method, high results are obtained whenever chlorides, sulphocyanates, or ferrocyanates are present.

The New Method.

Briefly stated, the new method consists in titrating an ammoniacal cyanide solution containing a small quantity of dimethyl glyoxime, with a standard nickel ammonium sulphate solution until a permanent red precipitate is produced. The reactions involved are expressed by the equations:—



No permanent red precipitate of nickel dimethyl glyoxime is formed until all of the cyanide has been used up in the reaction expressed by the first equation. The ammoniacal cyanide solution is used, since free sulphuric acid hinders the precipitation of nickel dimethyl glyoxime.

Solutions Required.

1. *Standard nickel solution*, prepared by dissolving 15.3 grms. of nickel ammonium sulphate in water containing 2 cc. of concentrated sulphuric acid, diluting to 1 litre, and standardising as directed below.

2. *Dimethyl glyoxime solution*, prepared by dissolving 8.9 grms. of dimethyl glyoxime in 1 litre of 95 per cent alcohol.

Standardisation of Nickel Solution.

Unless the percentage purity of the nickel ammonium sulphate is known, the prepared nickel solution must be standardised as follows:—25 cc. portions are diluted with distilled water to 200 cc., treated with 0.2 gm. tartaric acid, and heated to boiling. Glyoxime solution sufficient to precipitate all of the nickel is then added. If the glyoxime solution has been made up according to the formula above, 30 cc. should be sufficient. After the addition of the glyoxime, the solution is made slightly alkaline with ammonia, boiled for two minutes, and then set aside to digest for one-half hour. The precipitate is caught on a tared Gooch crucible, washed with 200 cc. of hot water, dried for forty-five minutes at 120° C., and weighed. The weighed precipitate contains 20.31 per cent nickel. From the equations given above the hydrocyanic acid or the potassium cyanide titre of the solution can readily be calculated. If a chemically pure potassium cyanide is at hand, the above titres can be determined directly by titrating weighed portions as directed in the "Method of Analysis" which follows.

Method of Analysis for Alkali Cyanides.

Five grms. of the sample are dissolved in water and diluted to exactly 500 cc. Pipetted 50 cc. portions of this solution are diluted with an equal volume of water, treated with 1 cc. of ammonium hydroxide and 0.5 cc. of the dimethyl glyoxime solution, and then titrated with the standard nickel solution until a permanent red precipitate is produced. The colour play towards the end of the reaction resembles the methyl orange end point observed in titrating an alkaline solution with an acid solution. The nickel ammonium sulphate solution may be added rapidly at first, provided the cyanide solution is vigorously stirred; toward the end-point the addition should be slower and the stirring more rapid. If more than 0.5 cc. of glyoxime is used, the end-point shows a tendency to appear too soon unless the addition of the standard solution is slow and the agitation of the solution very brisk. The cyanide dilution may be varied without serious effect; however, the method works better when the volume is approximately 100 cc. A large excess of ammonium hydroxide delays the end-point; 1 to 5 cc. in the volume specified does no harm. A titration requiring 50 cc. of the standard solution costs one fifth of a cent.

In titrating solutions which contain hydrocyanic acid, a measured volume of solution is made alkaline with ammonium hydroxide and then treated as above.

Table I. shows the values obtained on different cyanide samples by the new method and by two of the older methods.

TABLE I.—Analyses by different Methods—Percentages HCN.

Sample.	Gravimetric method (a).	New method.	Liebig's method.
1. KCN	39.35	39.16	39.55
2. KCN	39.25	39.00	39.57
3. KCN	40.75	40.71	40.79
4. NaCN	33.58	33.55	33.70
5. HCN solution	0.59	0.595	0.60
6. Cherry laurel water..	0.050	0.050	0.051
7. Oil of bitter almond water	0.076	0.076	0.077

(a) Corrected for chlorides.

The results obtained by all three methods check closely on Samples 3, 4, 5, 6, and 7. The values on Samples 1 and 2 are not in such good agreement, but it is seen that the new method checks up the corrected gravimetric method better than does Liebig's method. Qualitative tests showed small amounts of sulpho-cyanates and ferrocyanides, both of which would cause high results in the gravimetric method and Liebig's method.

Table II. demonstrates the accuracy of the new method in the presence of possible impurities in commercial cyanide samples:—

TABLE II.—*Titration of Mixtures.*

(50 cc. of 1 per cent KCN solution used in each titration).

Reagent added.	Nickel ammonium sulphate ² required (cc.).	Percentage error.
None	49'45	—
1 grm. KCNO	49'45	—
1 grm. KCNS	49'46	+0'02
1 grm. K ₂ CO ₃	49'41	-0'08
10 grms. K ₂ CO ₃	49'55	+0'20
20 grms. K ₂ CO ₃	49'62	+0'34
1 grm. K ₂ SO ₄	49'43	-0'04
1 grm. NH ₄ Cl	49'42	-0'06
1 grm. NaCl	49'47	+0'04
1 grm. NH ₄ NO ₃	49'39	-0'12
1 grm. NaHCO ₃	49'42	-0'06
0'1 grm. KOH	49'5	—
1 grm. KOH	50'02	+1'15
0'3 grm. CaNCN	49'46	+0'02
0'1 grm. K ₄ Fe(CN) ₆ ..	49'48	+0'06
1 grm. K ₄ Fe(CN) ₆ ..	50'75	+2'63

This table demonstrates the remarkable freedom of the method from interfering substances. KOH and K₄Fe(CN)₆ interfere when present in large amounts; and the small quantities usually present in commercial cyanides have practically no effect at all.

Table III. shows the accuracy of the method in the presence of the double cyanides commonly used in electroplating.

TABLE III.—*Titration in presence of Double Cyanides.*

Double cyanide present.	KCN added.	KCN found.	Percentage error.
	Grm.	Grm.	
KAg(CN) ₂ ..	0'1208	0'1205	-0'25
KCu(CN) ₂ ..	0'1915	0'1906	-0'47
K ₂ Zn(CN) ₄ ..	0'3520	0'4612	+31'02

It is seen that the method gives only the "free" cyanide in silver and copper cyanide solutions. Experiments show that more than the free cyanide is obtained in zinc cyanide solutions, the end-point occurring when the Zn: KCN ratio is approximately 1:0'6. In copper and silver cyanide solutions Liebig's method works the same as the new method. In zinc cyanide solutions Liebig's method gives the total cyanide; that is, the free cyanide plus the cyanogen in the zinc double cyanide. Hannay's method gives the total cyanide in all three cases. This is a disadvantage because only the free cyanide is ordinarily desired.

Summary.

The new method for the determination of hydrocyanic acid and the alkali cyanides consists in making the cyanide solution ammoniacal, then adding a small amount of methyl glyoxime solution, and finally titrating this prepared solution with a standard nickel ammonium sulphate solution until a permanent red precipitate is produced. The preceding shows that the new method is accurate, free from ordinary interferences, usable in cloudy solutions, rapid, cheap, and of value in titrations of double cyanides.—*Journal of Industrial and Engineering Chemistry*, vi., No. 7.

Thermo-chemical Study of Hydrates of Manganese Sulphate.—M. de Forcrand.—The author's determinations of the heat of solution of anhydrous manganese sulphate and its hydrates give results which do not always agree with those of Thomsen. It appears that two isomers of the anhydrous salt exist—one prepared at 300° by the ordinary method, and the other in the cold by very slow efflorescence. Probably the first is a polymer, (SO₄Mn)_n, of the second. Similarly, two isomers of the mono- and dihydrate exist, and possibly of all the intermediate hydrates which can exist between the anhydrous salt and the tetrahydrate in each series.—*Comptes Rendus*, clix., No. 1.

NOTICES OF BOOKS.

An Introduction to the Study of Organic Chemistry. By H. T. CLARKE, D.Sc.(Lond.), F.I.C. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1914.

THIS book has been written especially for the use of candidates for the lower examination in organic chemistry in the Board of Education Examinations in Science and Technology, and also for medical students. The author's aim has been to give a general view of the whole field of organic chemistry without going into details, and in particular without describing practical work at all. The choice of material is to be regarded as more or less out of the author's hands, being determined by the syllabus of the examination, and he cannot therefore be justly criticised for the omission of such subjects as stereoisomerism, the alkaloids, &c., while discussing other matter which might well be passed over in an introductory course. The clear summary giving the chief reactions of the principal classes of compounds will be very useful to examination candidates, but the value of the book is seriously impaired by the incompleteness of the index, in which, for example, no mention is to be found of "ketone," "glycerin," "amido," and other familiar names, although they are alluded to in the text.

The Storage of Petroleum Spirit and Carbide of Calcium. By Major A. COOPER-KEY, C.B. London: Charles Griffin and Co., Ltd. 1914.

THIS little book is intended for the use of inspectors, for whose benefit the best means of administering the Petroleum Acts are thoroughly explained, and for motorists who wish to know something about the precautions which should be taken in storing and using petroleum spirit. No details of composition or mining are given, and the author has been guided in his choice of material by a consideration of the actual questions which have been submitted for official reply. The terms of licences are thoroughly discussed and future legislation is suggested. A chapter on carbide of calcium and acetylene is included, and the texts of the Petroleum Acts of 1871 and 1881 and of the subsequent statutory Orders and Rules are given in full.

The Metallurgy of the Non ferrous Metals. By WILLIAM GOWLAND, F.R.S., A.R.S.M. London: Charles Griffin and Co., Ltd. 1914.

THE metallurgy of the most important metals, excluding iron, is comprehensively treated in this book, which will be a useful standard text-book and work of reference for both advanced students and practical metallurgists. No trouble has been spared to make it complete and up-to-date, and only modern and well-established processes are included for description. The general principles of the processes are first discussed, and different types of furnaces, &c., are described. The special treatment of the individual metals is then explained in full. In each case accounts are given of the metal's physical and chemical properties, of the chief alloys and their applications, and of the processes employed in extraction from the ores. The chemistry of the changes involved is fully discussed, and copious details of the plant are included.

Clay and Pottery Industries. Volume I. of the Collected Papers from the County Pottery Laboratory, Staffordshire. By several Authors. Edited by J. W. MELLOR, D.Sc. London: Charles Griffin and Co., Ltd. 1914.

THIS volume may be regarded as the first fruits of the Stoke-on-Trent Pottery School, issued in commemoration of the opening of the new buildings. It contains the most important papers which have been written by the teaching

staff and members of the classes since 1900, edited by Dr. J. Mellor, who is by far the largest contributor. The papers are mostly on practical subjects, such as the analysis of clays, the chemical and physical changes in the firing of pottery and clays, the behaviour of some glazes in the glost oven, &c., and are well illustrated by reproductions of photographs and coloured plates. Some lectures delivered by Dr. Mellor to audiences and others on technical education and foreign competition, &c., contain sound practical advice, which deserves to be widely read and taken to heart by educationalists.

The Examination and Thermal Value of Fuel—Gaseous, Liquid, and Solid. By J. H. COSTE, F.I.C., and E. R. ANDREWS, F.I.C. London: Charles Griffin and Co., Ltd. 1914.

METHODS employed in the comparison and valuation of fuels are well described in this book, and the authors' wide experience of the examination of fuels has enabled them to produce a work of great practical value. It is intended to be suitable for those who have had but little experience in the use of chemical and physical apparatus and in laboratory manipulations generally, but it will undoubtedly be found most valuable by the well-trained man. Methods of sampling and the physical and chemical examination of all classes of fuels are treated in detail, and a separate section on calorimetry is provided. The book may be regarded as an authoritative work on fuel examination, and may be used with confidence, both for reference on disputed points and for descriptions of routine work.

Memorials of Henry Forbes Julian. By HESTER JULIAN. London: Charles Griffin and Co., Ltd. 1914.

THIS biography of the late Henry Forbes Julian contains interesting accounts of his work as a mining engineer in South Africa, Germany, and elsewhere. His travels in various parts of the world are graphically described, especially his visit with the British Association to South Africa in 1905. The general public will read with interest of the sayings and doings of the many eminent men who formed Forbes Julian's circle of acquaintances, and of the tragic end of his life in the foundering of the *Titanic*.

Electric Furnaces for Making Iron and Steel. By DORSEY A. LYON and ROBERT M. KEENEY. Washington: Government Printing Office. 1914.

THIS bulletin contains a historical review of the development of electric furnaces for making iron and steel, and discusses the problems which must be solved in order that the use of electric furnaces for smelting iron ores and producing pig-iron may be profitable on a commercial scale. Different types of furnaces are described in detail and compared with one another, and accounts are given of the practice of the European and American works which were visited by the author.

The Osmotic Pressure of Aqueous Solutions. By H. W. MORSE. Washington, D.C.: The Carnegie Institute. 1914.

THIS book contains the report on investigations made in the chemical laboratory of the Johns Hopkins University during the years 1899–1913, and describes fourteen years of fruitful work. The first period of four years was devoted exclusively to the problem of the manufacture of cells, and when the difficulties of elaborating the method of measuring osmotic pressure were appearing almost insurmountable the author was fortunate enough to obtain the assistance of the Carnegie Institute of Washington. The finally perfected method was applied to the measurement of the osmotic pressures over a wide range of concentration and temperature of cane-sugar, glucose, levulose, and mannite, and the full results and the conclusions to be drawn from them are given in the report.

CORRESPONDENCE.

PROFESSOR BATESON'S ADDRESS.

To the Editor of the Chemical News.

SIR,—In the letter that you were good enough to insert in your issue of August 21, mention is made of a statement that discoveries are developed abroad rather than in this country for reasons that are explained. It may be desirable for me to say that the statement in question was made in a leader of the *Chemical Trade Journal*, which looks after the commercial interests of Chemical Industry just as the *CHEMICAL NEWS* watches those of a scientific character.

In this connection allow me to refer to the great service you have done in these troubled times by completely reporting Prof. Bateson's Address given at Melbourne and Sydney. It seems not too much to say that were we at peace this deliverance would have caused as much discussion as Huxley's Belfast one did, though certainly with less acerbity. The reversal of the hypothesis of development and the subversion of the Darwinian theory with a strong blow at the Malthusian surely constitute an epoch-making event. This matter that your Journal so conveniently enshrines must perforce come under discussion later on, when reading war news does not take up most of our spare time.—I am, &c.,

F. J. R. CARULLA.

Derby, September 3, 1914.

PATENT AND TRADE MARKS ACT OF 1907.

To the Editor of the Chemical News.

SIR,—I am interested in the proposal which is on foot to nullify the operation of the Patents and Trades Marks Act of 1907. It will be recollected that this Act made the working of foreign patents compulsory in the United Kingdom if their validity here was to be maintained. As a result, works have, I believe, been erected and are in operation in this country for the express object of manufacture under such patents, though doubtless in some cases other manufactures were subsequently introduced in such works.

I shall be obliged if any of your readers could furnish me with some particulars of firms whose existence in Great Britain has been brought about by this Act.—I am, &c.,

ALEX. E. TUCKER.

Birmingham Central Laboratories,
55, Station Street, Birmingham,
September 7, 1914.

THE INSTITUTION OF CHEMICAL TECHNOLOGISTS.

To the Editor of the Chemical News.

SIR,—I desire, with your permission, to point out that the Institution of Chemical Technologists is willing to put British technical chemists and British chemical manufacturers in touch with each other, in view of a probable early increase in manufacturing chemistry in this country and the Dominions.

I wish to emphasise most strongly that this Institution is concerned only with British manufacturers and British technical chemists. It has been founded expressly and solely for the benefit of British subjects; it does not admit any but British subjects to its membership.—I am, &c.,

J. WILBERFORCE GREEN, Secretary.

30, Victoria Street, Westminster, S.W.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 26, July 29, 1914.

Dimethylallylacetophenone and its Oxidation Products.—J. Meyeringh and A. Haller.—When dimethylallylacetophenone is oxidised with potassium permanganate in the cold the glycol 4-benzoyl-4-methyl-2,1-pentane diol and 4-benzoyl-4-methyl- α -oxyvalerianic acid are formed. The glycol is identical with that obtained by Mme. Ramart-Lucas and A. Haller by heating oxypropylene-dimethylacetophenone with water under pressure. Under the influence of acid chlorides, acids, and phenylisocyanate, the same glycol loses water and condenses with itself, giving the dimer of oxypropylene-glycol, fusing at 214°. In presence of pyridine a monobenzoyl derivative of the glycol is always obtained. When allyldimethylacetophenone is oxidised at a higher temperature ketoglycol is formed.

Bromination of Cobalt and Nickel in presence of Ethyl Oxide.—F. Ducelliez and A. Raynaud.—When powdered cobalt is treated with dry bromine at the ordinary temperature in presence of anhydrous ether a green substance is deposited. If this is heated to drive off the ether, pure anhydrous bromide of cobalt is obtained. If the bromine and cobalt are employed in the proportions required by the formula Co_2Br (with a slight excess of halogen), and a large excess of ether is avoided, an intermediate product of formula $\text{CoBr}_2(\text{C}_4\text{H}_{10}\text{O})$ may be isolated. Analogous results are obtained with nickel, but the intermediate product is more stable. When heated it yields the anhydrous bromide NiBr_2 .

Revision of the Atomic Weight of Uranium.—O. Hönlischmid.—The number accepted as the atomic weight of uranium depends upon the determinations of Richards and Merigold who analysed uranium bromide. Their experiments were performed in vessels of glass and porcelain, which are attacked by bromine and by the bromide itself, which would thus contain small quantities of alkaline bromide and oxybromide. To avoid the formation of these impurities the author used a silica vessel, in which he heated a mixture of UO_2 and sugar carbon in bromine vapour. In a first series of experiments the uranium bromide was sublimed and then distilled, fused, and solidified in bromine vapour. The bromide was then analysed by Richards's method, the result being numbers which ranged from 238.07 to 238.12, the mean being 238.09. In a second series of experiments the sublimed bromide was distilled, fused, and solidified in a current of nitrogen; the results obtained ranged from 238.15 to 238.18, the mean value being 238.17. In the first series the bromine is present in excess, and the value obtained is the lower limit of the atomic weight of uranium. The second series gives a very pure bromide, and the mean of the results, viz., 238.175, is the most probable value for the atomic weight of uranium.

Vol. clx., No. 1, July 6, 1914.

Influence of Tellurium upon the Sensitiveness of Selenium to Light.—M. Abonnenc.—The author prepared selenium cells, in which the selenium contained known varying amounts of tellurium, and exposed them to different kinds of light. He found that the sensitiveness towards green and white light diminishes as the percentage of tellurium is increased from 1 to 7, while the sensitiveness towards red light passes through a maximum.

Catalytic Action of Copper Oxide on the Combination of Oxygen and Hydrogen.—Jacques Joannis.—At 300° compact iron is not a catalyst for detonating gas; an oxide is formed which is not reducible at this temperature.

At 200° copper is oxidised by detonating gas, and the oxide formed is a catalyst for the gas. At 300° it induces the total combination of the gas. The tension of the water vapour formed seems to take an important part in the catalysis.

Manganese Sulphide. Estimation of Manganese.—A. Villiers.—Manganese sulphide exists in two different forms, pink and green; the latter is much the denser and less oxidisable, and can be washed quickly. In determining manganese as sulphide it is therefore preferable to obtain the green form, and this may be done at a temperature of about 100° if ammonia is added to the warm liquid before the addition of ammonium sulphhydrate. The sulphide is then obtained in the form of a very dense precipitate, sometimes as dark green or nearly black crystals.

Hydrogenations by Sodammonium.—P. Lebeau and M. Picon.—Sodammonium can be used to hydrogenate various hydrocarbons. Thus, anthracene is converted into the dihydride, and diphenyl into the tetrahydride. The equation is $\text{C}_{14}\text{H}_{10} + (\text{NH}_3\text{Na})_2 = \text{C}_{14}\text{H}_{12} + 2\text{NH}_2\text{Na}$. Sodammonium does not hydrogenate amylene or the benzene hydrocarbons, or terpinene, terpinolene, &c. With fluorene and indene no hydrogenation occurs, but sodium compounds are formed, while certain heterocyclic nuclei are capable of undergoing both reactions.

Preparation of Derivatives of α -Pyrone from Oxalacetic Ether.—H. Gault.—When oxalocitric lactone, obtained by Claisen's method from oxalacetic ether, is treated with hydrochloric acid and boiled, the lactonic chain is opened, and oxalocrotonic acid is formed by saponification, elimination of two molecules of carbonic anhydride and dehydration. The oxalocrotonic acid then undergoes cyclisation, giving rise to 1,2-pyrone-6-carboxylic acid.

Allyl and Methylallyl, Propyl and Methylpropylcyclohexanones.—R. Cornubert.—The author has studied the preparation of cyclohexanols from the corresponding ketones by means of sodium and absolute alcohol, and the transformation of allylcyclo into propylcyclohexanones by catalytic hydrogenation in presence of nickel. He finds that catalysts are characterised by selective action, being capable of hydrogenating some substances and not others. For substances which are isomeric and very similar in constitution there is no general law representing mathematically the absorption of hydrogen as a function of the time. Some nickels induce the rapid saturation of one or two double bonds and slowly saturate others. The propylcyclohexanones can be obtained by the hydrogenation of the corresponding allylcyclohexanones.

Syntheses of mixed Organometallic Derivatives of Zinc. γ -Chlor Ketones.—Henri Wohlgemuth.—By the action of the mixed organometallic derivatives of zinc a γ -halogen ketone can be obtained from the chloride of a γ -halogen acid. The acyclic γ -chlor ketones are readily hydrolysed when boiled with ten times their weight of water, giving the corresponding γ -ketone alcohols, which are characterised by their readiness to lose water, being converted into $\alpha\beta$ -dihydrofuranic compounds. When reduced with sodium amalgam they give γ -glycols.

Dioxytriazines.—J. Bougault.—Dioxytriazines can very readily be obtained by the dehydration of the semicarbazones of α -ketonic acids, the dehydration being effected by the action of hot very dilute alkalis. They are crystallised compounds, insoluble in water and soluble in boiling alcohol. They are acids, giving salts and ethers, the latter being readily obtained by letting the monopotassium salt act on an alkyl iodide in solution in the corresponding alcohol.

NOTES AND QUERIES.

Hardening Oils.—Can any reader put me in communication with the firm operating the process of hardening oils by hydrogenising?—T. E. TROLLOPE.

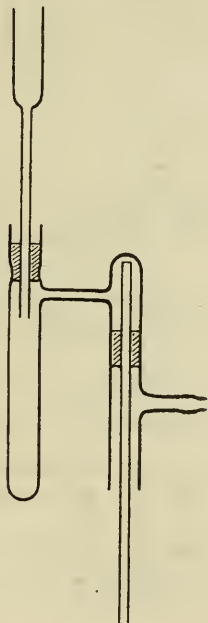
THE CHEMICAL NEWS.

Vol. CX., No. 2862.

NEW FORM OF INTERMITTENT SYPHON.

By W. A. BRADBURY.

DURING the course of some experiments it was required automatically to flush the beads contained in an absorption tube. As the amount of liquid to be used was only about 50 cc. an hour, it meant that for a constant delivery the feed could only be in small drops, and at this rate of delivery it was not sufficient for flushing the beads, as a quantity of at least 2 cc. each time was necessary to swill the beads. It was therefore decided to use an intermittent syphon to give the necessary flush. As the absorption tube was being worked in conjunction with Volhard's flasks and an aspirator, an ordinary intermittent syphon did not answer the purpose. In the first place it was difficult to make one to give such a small flush, and



secondly, the constant passage of air through the syphon was a great objection to it. To overcome this difficulty we designed a syphon which answered the purpose perfectly, and is shown by the sketch. This allows the pull of the aspirator to be perfectly counterbalanced by altering the position of the feeding funnel; and also we can get a variable flush by altering the diameter of the feeding tube or pushing it further into the outer tube. By using a Mariotte's bottle with a capillary tube, or, better still, a narrow glass tube with a stopcock and packed with cotton-wool as the delivery tube, we have an arrangement which gives a constant feed in drops, with a flush delivery by the syphon.

An important point to be attended to is to have the delivery tube of the syphon as small as possible, but large enough to give a quick flush, and to have the end of the tube quite close up to the top of the outside tube of the syphon.

ESTIMATION OF SULPHUR IN MOTOR SPIRITS.

By W. A. BRADBURY and F. OWEN.

IN searching for a method to enable us to estimate the sulphur in motor spirits, we found that a very large amount of work has been done, and a very varied assortment of apparatus devised for its solution. Our experience leads us to conclude that the fact of having such a diversity of method and apparatus points to the unsatisfactory results which must have been obtained.

According to Hicks's "Mineral Oil Testing," p. 60, "After a long series of tests, made under the supervision of Sir Boverton Redwood, it was concluded that the bomb calorimeter was the most trustworthy apparatus for all oils."

As the prospective number of samples to be tested did not warrant the purchase of a bomb calorimeter, we decided to adopt the method advised by Irwin for the determination of sulphur in benzol for use in gas works. He

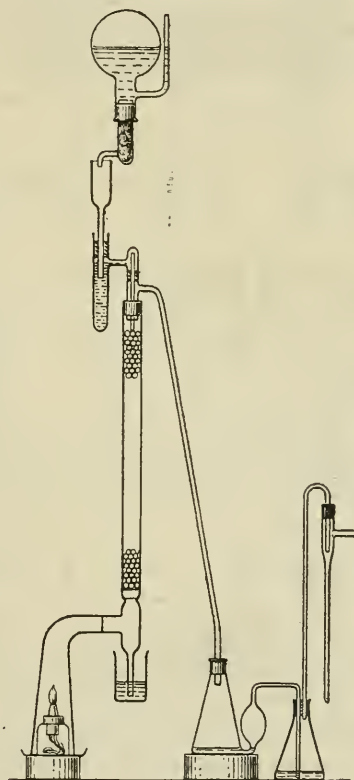


FIG. 1.

made use of a slightly modified Referee apparatus, and he describes his method as follows:—"I take away the burner and replace it by a spirit-lamp capable of holding 100 cc. of spirit. Of the benzol to be tested I carefully measure out 10 cc. into the spirit-lamp, and then add to it 90 cc. of pure alcohol or methylated spirit, shake the two together, and light the lamp. Round the lamp I place several pieces of fresh carbonate of ammonia, and in all respects proceed exactly as in the test for sulphur in coal-gas. After the end of the operation the whole of the apparatus is washed with distilled water, a little bromine water added, and the sulphuric acid estimated in the usual way. Duplicate tests for a Staffordshire benzol gave

0.44 per cent and 0.45 per cent (methylated spirit 0.01 per cent).

Our tests with this apparatus were not satisfactory. Although it may happen that two consecutive tests will correspond, it is more a coincidence than due to the reliability of the method. The average of the results obtained is 71 per cent of the theoretical. The difference between the maximum and minimum results being 29 per cent. It may be stated here that we depended upon the estimation of a known weight of carbon disulphide in methylated spirit to test the reliability of the method and apparatus.

Owing to the inconvenience of washing out the Referee apparatus, we decided to endeavour to make a more satisfactory arrangement. The new apparatus ultimately assumed the form as shown by Fig. 1. It is practically an elongated narrow form of the Referee cylinder, with a new form of intermittent syphon by which the beads were automatically and regularly flushed during the experiment.

The results obtained with this apparatus were as unsatisfactory as with the Referee. The average result was 79 per cent of the theoretical. The difference between the maximum and minimum result being 20 per cent.

We thought that owing to the high sp. gr. of sulphurous acid, and the probability of eddy currents being

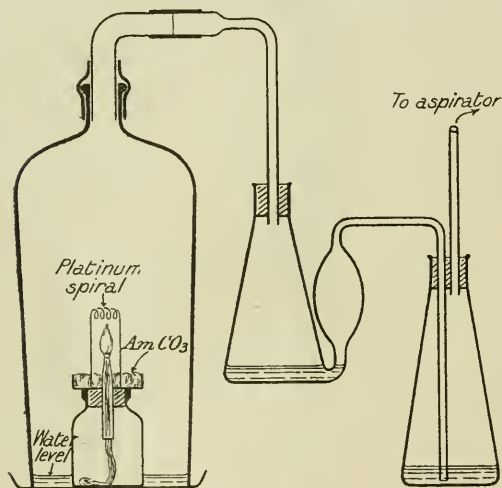


FIG. 2.

formed in the trumpet tube, that some of the products of combustion were being lost from the mouth of the tube. We therefore arranged a water seal to the trumpet. On starting the aspirator, the water was drawn into the trumpet and the air bubbled through the water. The value of this seal was proved in the next tests, as in every case the sealing water contained sulphuric acid. From the summary of results it will be seen that the average result when using the seal was 79.7 per cent against 78.8 per cent without the seal. The variation between the maximum and the minimum result was 14.2 per cent with the seal, against 26 per cent without the seal. Various liquids have been used for flushing the beads and marbles, viz., water, permanganate, bromine, ammonia, perhydrol.

The next series of experiments were made by absorbing the gases of combustion in Shead's flasks, using perhydrol as the absorbing fluid. The average result obtained with this apparatus was 87.7 per cent of the theoretical, and the difference between the maximum and minimum test was 17 per cent. Varying amounts of CS₂ and spirit, and different times of burning off—from two and a-half hours to eight hours—all yielded about equal results.

As the water seal practically converts the combustion

chamber into a closed vessel, and as the last flask in the arrangements was in all the tests free from sulphuric acid, it follows that all the sulphuric acid which has been formed has been estimated. It must therefore be concluded that the variation in the results is due in some way to defective combustion, and for some reason the combustion is best when using the absorbing flasks—that it is not due to the size of the combustion chamber is proved by the fact that equal results have been obtained when the combustion has been effected in a piece of Jena combustion tube, the ordinary trumpet tube of the Referee apparatus, or in a Winchester quart bottle with the bottom cut off.

The best results were obtained in the Shead's flasks, but the result of a single test cannot be considered correct

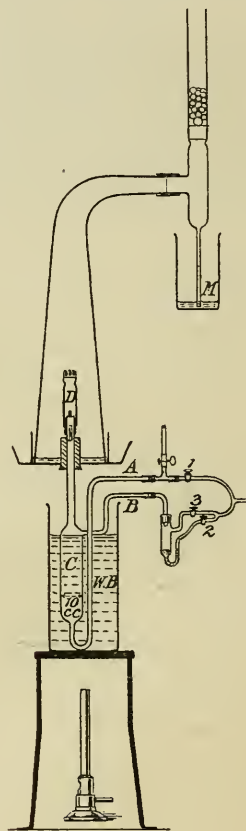


FIG. 3.

within 21 per cent. The error is practically the same both for carbon disulphide and motor benzols.

A curious fact is that three tests of methylated spirit in the Referee apparatus gave identical results.

An example of the elusiveness of the whole matter is shown in the testing of sample 2 of benzol. Eight tests were made of this sample, and each consecutive test gave a lower result, until, on using the apparatus Fig. 2 the result jumped to 13 per cent higher than the previous maximum. The following are the results in the order of testing:—

Referee	259	grains sulphur per gallon.
New form	258	" "
New form	231	" "
Flasks	198	" "
New form	193	" "
Referee	119	" "
Referee	129	" "
Fig. 2	296	" "

Other tests with this apparatus show that there is no advantage gained by it.

Having arrived at the conclusion that the irregularities of the results are due to imperfect combustion, our object was now to overcome this difficulty, and in our next experiments the spirit-lamp was displaced and a carburettor *c* (Fig. 3) adopted. Air is carburetted by being blown through the motor spirit to be tested, and an extra supply of air to complete the combustion is mixed with it. Attached to the extra air tube is an auxiliary carburettor which contains a pure benzol or petrol, and is used to form a pilot light until the trumpet is connected up to the absorbing tube; loss of motor spirit to be tested is thus prevented during the time the connections are being made. Attached to the carburetting tube is a $\frac{1}{2}$ piece, to the branch of which is connected by rubber tube a piece of glass tube about 5 cc. capacity; the rubber tube is closed by a clip and the glass tube by a cork. This tube is filled with turpentine and is used for sweeping out the last traces of motor spirit from the carburettor *c* at the end of the experiment. The tubes *D* and *E* are fitted with gauze caps, and a platinum spiral is fitted over *D*.

The following is the method of working:—10 cc. of the benzol or petrol to be tested is filled into *c*. All the taps are closed and the motor blower set on. The perhydrol solution in the Mariotte's bottle, Fig. 1 (150 cc. water, 6 cc. perhydrol), is now allowed to flow at the rate of 100 cc. per hour. When the beads have become wet, and the end of the tube *M* sealed, tap 2 is opened, air bubbles through the pure benzol and the mixture is ignited at *D*; tap 3 is then opened, and the extra air supply is regulated to form a perfect Bunsen burner flame at *D*, and the platinum spiral is raised to its strongest point of incandescence. The flame is kept low, about half an inch high. The trumpet tube is now placed over the light, and rests on the tray and in the water seal; the small end is then connected up to the absorbing tube (Fig. 1), but without the flasks and aspirator. Tap 1 is now opened and tap 2 gradually closed. Taps 1 and 3 are regulated to give the light required.

When about one-half of the spirit has burnt off, the water-bath is gradually heated to 150° to 160° F. The taps 1 and 3 will probably require attention at this point to keep the platinum spiral at the proper state of incandescence. When the spirit has been reduced to a few drops, the clip 4 is opened and about 1 cc. of turpentine admitted to *c*, and the operation is repeated until all the turpentine has been burnt off; all the benzol is thus swept out of *c* and burnt.

At the end of the operation, the trumpet, tray, and absorbing tube are washed, and the sulphuric acid estimated in the usual way.

A motor benzol which had yielded by the Shead's flasks 231 grains and 239 grains of sulphur per gallon respectively, gave by the new method 240, 224, 230, 228, 240 grains sulphur per gallon. A carbon disulphide yielded 90 per cent, 94·2 per cent, 95·5 per cent of the theoretical.

These tests seem to confirm our conclusion from the previous set of experiments, that faulty combustion was the cause of the variation in the results.

SUMMARY OF RESULTS.

Carbon Disulphide.

Average for Referee apparatus..	71 per cent of theoretical
" " New form (Fig. 1) ..	79 " "
" " Shead flasks ..	87·7 " "

Difference between the maximum and minimum test—

Referee ..	29 per cent.
New form (Fig. 1) ..	14 per cent.
Shead flasks ..	17 per cent.

Deficiency from the theoretical—

	Max test. Per cent.	Min. test. Per cent.
Referee ..	14	50
New form (Fig. 1) ..	12	26
Shead flasks ..	4	21

	Per cent.	Per cent.	Per cent.
Carburettor (Fig. 3) ..	90	94·2	95·5

Benzol.

No. of Sample.	No. of test	Apparatus.	Per cent sulphur.	Grains per gal.	Diff. (per cent) Max. and Min
1.	1.	Referee ..	0·337	209	
	2.	Referee ..	0·278	172	17·7
2.	1.	Referee ..	0·416	258	
	2.	Referee ..	0·175	118	54·3
	3.	Referee ..	0·182	130	
3.	1.	New ..	0·415	257	
	2.	New ..	0·373	231	
	3.	New ..	0·312	193	25·0
3.	1.	Shead's ..	0·317	198	
	1.	Fig. 2 ..	0·474	294	
3.	1.	Shead's ..	0·478	296	
	2.	Referee ..	0·336	208	29·7
	3.	New ..	0·459	284	
4.	1.	Shead's ..	0·385	240	
	2.	Shead's ..	0·373	232	
1.	1.	Fig. 3 ..	0·360	224	6·6
	2.	Fig. 3 ..	0·368	228	
3.	1.	Fig. 3 ..	0·372	230	
	4.	Fig. 3 ..	0·385	240	

ON BOILING-POINTS IN HOMOLOGOUS SERIES.

By S. SUGDEN.

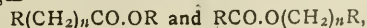
(Concluded from p. 153).

TABLE IV. gives the observed and calculated values for the alkyl halides. For all three series *a* has the same value as that already found for the paraffins. If *b* is plotted against the atomic weights of the halogens a straight line is obtained.

Table V. gives the observed and calculated values for the alkyl hydrosulphides. For these substances the constant *a* has the same value as for the closely related alcohols.

Tables VI. and VII. show the application of the new formula to the aldehydes and amines. These substances require the same value for *a* as the fatty acids. The similarity of structure between the aldehydes and acids is obvious, but the occurrence of the amines in this group is not easy to explain. The writer can only suggest that all three classes of substances contain two unsaturated valencies at the end of the chain.

In the case of the esters a number of complete series are known, including many metameric compounds. Of course a formula of this type does not distinguish between such substances, and it seemed advisable to study the effect of the symmetry of the molecule upon the constants of the formula. The esters were therefore arranged in series of the types—



so that all the members of a given series had approximately the same degree of asymmetry. When this was done it was found that the constant *a* was the same for all the esters, while *b* increased as *n* increased. The isomeric compounds of the above two types were found to have almost the same boiling-point, so these two series are considered together.

TABLE IV.—Allyl Halides, R.X.

RCl	a = 41.01	b = -256.0
RBr	a = 41.01	b = -1197.0
RI	a = 41.01	b = -2038.0

R.	RCl.			RBr.			RI.		
	T (obs.). ° Abs.	T (calc.). ° Abs.	Diff.	T (obs.). ° Abs.	T (calc.). ° Abs.	Diff.	T (obs.). ° Abs.	T (calc.). ° Abs.	Diff.
CH ₃	249.3	247.3	-2.0	277.5	273.7	-3.8	315.8	314.9	-0.9
C ₂ H ₅	285.5	287.1	+1.6	311.4	309.9	-1.5	345.5	345.9	+0.4
C ₃ H ₇	319.0	321.8	+2.8	343.8	345.0	+1.2	375.5	375.0	-0.5
C ₄ H ₉	351.0	352.8	+1.8	374.0	372.0	-1.1	403.0	402.5	-0.5
C ₅ H ₁₁	379.6	381.3	+1.7	402.5	401.5	-1.0	429.0	428.3	-0.7
C ₆ H ₁₃	406.0	406.0	0.0	429.0	427.7	-1.3	452.0	452.7	+0.7
C ₇ H ₁₅	433.0	432.0	-1.0	452.0	453.2	+1.2			
C ₈ H ₁₇	457.0	455.0	-2.0	474.0	477.0	+3.0			
Mean diff. = 1.61°				Mean diff. = 1.89°			Mean diff. = 0.62°		

TABLE V.—Hydrosulphides, R.S.H.

a = 34.30. b = 261.8.

R.	T (obs.). ° Abs.	T (calc.). ° Abs.	Diff.
CH ₃	279.0	281.7	+2.7
C ₂ H ₅	309.0	311.3	+2.3
C ₃ H ₇	340.5	339.0	-1.5
C ₄ H ₉	370.5	305.0	-5.5
Mean diff. = 3.00°			

TABLE VI.—Aldehydes R.CHO.

a = 35.93. b = 301.0.

R.	T (obs.). ° Abs.	T (calc.). ° Abs.	Diff.
H	252.0	255.4	+3.4
CH ₃	293.8	289.1	-4.7
C ₂ H ₅	322.0	320.1	-1.9
C ₃ H ₇	347.0	349.0	+2.0
C ₄ H ₉	376.0	376.0	—
C ₅ H ₁₁	400.9	401.3	+0.4
C ₆ H ₁₃	428.0	425.5	-2.5
Mean diff. = 2.13°			

TABLE VII.—Amines R.NH₂.

a = 35.93. b = 318.0.

R.	T (obs.). ° Abs.	T (calc.). ° Abs.	Diff.
CH ₃	267.0	260.7	-6.3
C ₂ H ₅	291.7	293.5	+1.8
C ₃ H ₇	322.7	324.1	+1.4
C ₄ H ₉	348.5	352.5	+4.0
C ₅ H ₁₁	376.0	379.1	+3.1
C ₆ H ₁₃	402.0	404.1	+2.1
C ₇ H ₁₅	427.0	427.9	+0.9
Mean diff. (°C.) = 2.80°			

TABLE VIII.—Esters R.CO.OR.

a = 33.20. b = 283.7.

R.	T (obs.). ° Abs.	T (calc.). ° Abs.	Diff.
CH ₃	330.2	327.3	-2.9
C ₂ H ₅	371.8	375.3	+3.5
C ₃ H ₇	415.7	418.5	+2.8
C ₄ H ₉	458.8	458.4	-0.4
C ₅ H ₁₁	—	495.4	—
C ₆ H ₁₃	—	530.2	—
C ₇ H ₁₅	562.8	563.1	+0.3
Mean diff. = 1.98°			

TABLE IX.—Esters RCO.OCH₂R and RCH₂COOR.

a = 33.20. b = 289.5.

R.	T (calc.). ° Abs.	R.CO.OCH ₂ R.		RCH ₂ COOR.	
		T (obs.). ° Abs.	Diff.	T (obs.). ° Abs.	Diff.
H	301.6	304.9	-3.3	—	—
CH ₃	352.4	350.15	+2.25	352.7	-0.3
C ₂ H ₅	397.7	395.3	+2.4	392.9	+4.8
C ₃ H ₇	439.0	438.7	+0.3	440.5	-1.5
C ₄ H ₉	477.4	476.7	+0.7	477.3	+0.1
C ₅ H ₁₁	512.7	—	—	—	—
C ₆ H ₁₃	546.7	547.6	-0.9	—	—
C ₇ H ₁₅	578.6	578.9	-0.3	—	—
Mean diff. = 1.45°				Mean diff. = 1.68°	

TABLE X.—Esters RCOO(CH₂)₂R and R(CH₂)₂COOR.

a = 33.20. b = 291.0.

R.	T (calc.). ° Abs.	RCOO(CH ₂) ₂		R.R(CH ₂) ₂ COOR.	
		T (obs.). ° Abs.	Diff.	T (obs.). ° Abs.	Diff.
H	327.8	327.3	+0.5	—	—
CH ₃	375.7	374.55	+1.15	375.75	-0.05
C ₂ H ₅	418.7	418.4	+0.3	417.7	+1.0
C ₃ H ₇	458.5	457.8	+0.7	458.5	—
C ₄ H ₉	495.4	496.8	-1.4	498.1	-2.7
C ₅ H ₁₁	530.1	532.4	-2.3	—	—
C ₆ H ₁₃	563.0	563.4	-0.4	—	—
Mean diff. = 0.96°				Mean diff. = 0.94°	

TABLE XI.—Esters RCOO(CH₂)₃R and R(CH₂)₃COOR.

a = 33.20. b = 317.0.

R.	T (calc.). ° Abs.	RCOO(CH ₂) ₃ R.		R(CH ₂) ₃ COOR.	
		T (obs.). ° Abs.	Diff.	T (obs.). ° Abs.	Diff.
H	354.4	353.9	+0.5	—	—
CH ₃	399.0	397.5	+1.5	400.3	-1.3
C ₂ H ₅	439.9	—	—	439.6	+0.3
C ₃ H ₇	477.9	478.1	-0.2	479.4	-1.5
C ₄ H ₉	512.6	516.6	-4.0	513.5	-0.9
C ₅ H ₁₁	546.2	548.2	-2.0	—	—
Mean diff. = 1.64°				Mean diff. = 1.00°	

TABLE XII.—Esters $\text{RCOO}(\text{CH}_2)_4\text{R}$ and $\text{R}(\text{CH}_2)_4\text{COOR}$.

$a = 33.20.$
 $b = 354.2.$

R.	T (calc.). ° Abs.	$\text{RCOO}(\text{CH}_2)_4\text{R}.$		$\text{R}(\text{CH}_2)_4\text{COOR}.$	
		T (obs.).	Diff.	T (obs.).	Diff.
		° Abs.		° Abs.	
H..	380.0	379.9	+0.1	—	—
CH ₃	421.7	420.6	+1.1	422.6	-0.9
C ₂ H ₅	460.3	—	—	460.1	+0.2
C ₃ H ₇	496.2	498.2	-2.0	497.7	-1.5
C ₄ H ₉	530.1	533.2	-3.1	—	—
Mean diff. = 1.58°		Mean diff. = 0.87°			

TABLE XIII.—Esters $\text{R.COO}(\text{CH}_2)_5\text{R}$ and $\text{R}(\text{CH}_2)_5\text{COOR}$.

$a = 33.20.$
 $b = 384.0.$

R.	T (calc.). ° Abs.	$\text{RCOO}(\text{CH}_2)_5\text{R}$		$\text{R}(\text{CH}_2)_5\text{COOR}$	
		T (obs.).	Diff.	T (obs.).	Diff.
		° Abs.		° Abs.	
H..	403.2	403.4	-0.2	—	—
CH ₃	442.9	442.2	+0.7	445.1	-2.2
C ₂ H ₅	479.8	481.0	-1.3	478.8	+1.0
C ₃ H ₇	513.9	515.2	-1.3		
		Mean diff. = 0.88°		Mean diff. = 1.60°	

A similar plan was pursued with the ethers. Owing to lack of data only the first two series are given as they are the only series containing over three members.

TABLE XIV.—Ethers R.O.R.

$a = 32.20. \quad b = 136.0.$

R.	T (obs.). ° Abs.	T (calc.). ° Abs.	Diff.
CH_3	249.35	249.3	-0.05
C_2H_5	307.6	310.3	+2.7
C_3H_7	363.7	362.9	-0.8
C_4H_9	413.9	409.8	-4.1
C_5H_{11}	—	452.9	—
C_6H_{13}	—	493.2	—
C_7H_{15}	534.9	531.2	-3.7
C_8H_{17}	564.7	567.1	+2.4
Mean diff. = 2.29°			

TABLE XV.—Ethers R.O. CH_2R .

$a = 32.20. \quad b = 128.3.$

R.	T (obs.). ° Abs.	T (calc.). ° Abs.	Diff.
CH_3	283.8	281.2	-2.6
C_2H_5	336.0	337.9	+1.9
C_3H_7	390.1	387.8	-2.3
C_4H_9	—	433.3	—
C_5H_{11}	—	475.6	—
C_6H_{13}	—	514.6	—
C_7H_{15}	551.8	552.0	+0.2
Mean diff. = 1.75°			

TABLE XVI.—Alkyl Cyanides, $\text{R.C}\equiv\text{N}$.

$a = 34.84. \quad b = 827.0.$

R.	T (obs.). ° Abs.	T (calc.). ° Abs.	Diff.
CH_3	354.6	354.0	-0.6
C_2H_5	370.1	372.2	+2.1
C_3H_7	391.5	391.9	+0.4
C_4H_9	413.4	411.7	-1.7
C_5H_{11}	—	431.3	—
C_6H_{13}	449.5	450.4	+0.9
C_7H_{15}	469.7	468.8	-0.9
C_8H_{17}	488.0	486.9	-1.1
Mean diff. = 1.10°			

TABLE XVII.—Benzene Hydrocarbons, $\text{R.C}_6\text{H}_5$.

$a = 45.71. \quad b = 191.42.$

R.	T (obs.). ° Abs.	T (calc.). ° Abs.	Diff.
H..	353.5	354.2	+0.7
CH_3	383.6	382.9	-0.7
C_2H_5	409.0	408.5	-0.5
C_3H_7	431.5	432.6	+0.9
C_4H_9	453.0	454.4	+1.4
C_5H_{11}	474.5	474.6	+0.1
Mean diff. = 0.72°			

TABLE XVIII.—Normal Secondary Alcohols.

$a = 33.50. \quad b = 712.0.$

Formula.	T (obs.). ° Abs.	T (calc.). ° Abs.	Diff.
$\text{C}_3\text{H}_7\text{OH}$	355.0	354.2	-1.3
$\text{C}_4\text{H}_9\text{OH}$	373.0	374.4	+1.4
$\text{C}_5\text{H}_{11}\text{OH}$	392.0	394.2	+2.2
$\text{C}_6\text{H}_{13}\text{OH}$	409.0	412.8	+3.8
$\text{C}_7\text{H}_{15}\text{OH}$	437.5	432.4	-5.1
$\text{C}_8\text{H}_{17}\text{OH}$	452.0	450.5	-1.5
Mean diff. = 2.55°			

TABLE XIX.—Nitro Paraffins, R.NO_2 .

$a = 32.75. \quad b = 890.0.$

R.	T (obs.). ° Abs.	T (calc.). ° Abs.	Diff.
CH_3	374.0	372.8	-1.2
C_2H_5	387.5	389.2	+1.7
C_3H_7	404.0	406.6	+2.6
C_4H_9	424.5	424.0	-0.5
Mean diff. = 1.50°			

TABLE XX.—Olefines $\text{R.CH}=\text{CH}_2$.

$a = 22.89. \quad b = 13.47.$

R.	T (obs.). ° Abs.	T (calc.). ° Abs.	Diff.
H..	170.5	171.2	+0.7
CH_3	222.8	221.8	-1.0
C_2H_5	268.0	268.3	+0.3
C_3H_7	312.5	312.2	-0.3
Mean diff. = 0.58°			

The constants used in the preceding tables are brought together in Table XXI.

The advantages claimed for the new formula are:—

(a). It is the only formula known which will represent the boiling-points of all the members of the series already tabulated. In the preceding tables 169 boiling-points have been calculated with an average error of 1.63°. The greatest difference between the observed and calculated values of the boiling-point are 6.3° C. for methylamine, 5.5° for butyl hydrosulphide, and 5.1° C. for the secondary heptyl alcohol. From the general agreement of the rest of these series it appears probable that the values of the "observed" boiling-points of these three substances used are a few degrees in error. In every other case the difference between the observed and calculated values of the boiling-point is less than 5° C. Since the boiling-points of metameric substances may differ by 10° this is as much as can be expected from a formula of this type.

(b). The formula is simple in mathematical form, and contains only two arbitrary constants.

(c). The use of this formula brings to light several relationships between the constants for series of closely related substances. Such relationships are not apparent when the constants obtained by the use of other formulæ, e.g., Walker's, Boggio Lera's, &c., are considered.

The disadvantage it suffers from is that it gives no account of the difference in boiling-point of metameric substances.

TABLE XXI.

Series.	General formula.	a.	b.
Benzene hydrocarbons..	R.C ₆ H ₅	45.71	-91.42
Paraffins	R.H	41.01	-205.1
Alkyl chlorides .. .	R.Cl	41.01	-256.0
Alkyl bromides .. .	R.Br	41.01	-1197.0
Alkyl iodides .. .	R.I	41.01	-2038.0
Aldehydes .. .	R.CHO	35.93	+301.0
Fatty acids .. .	R.CO ₂ H	35.93	+881.0
Amines .. .	R.NH ₂	35.91	+318.0
Alkyl cyanides .. .	R.CN	34.84	+827.0
Normal primary alcohols	R.OH	34.50	+805.5
Hydrosulphides .. .	R.SH	34.20	+261.8
Normal secondary alcohols	RCH(OH)CH ₃	33.50	+712.0
	R.CO.OR	33.20	+283.7
	RCH ₂ COOR	33.20	+289.5
	and RCOOCH ₂ R		
	R(CH ₂) ₂ COOR	33.20	+291.0
	and RCOO(CH ₂) ₂ R		
	R(CH ₂) ₃ COOR	33.20	+317.0
	and RCOO(CH ₂) ₃ R		
	R(CH ₂) ₄ COOR	33.20	+354.2
	and RCOO(CH ₂) ₄ R		
	R(CH ₂) ₅ COOR	33.20	+384.0
	and RCOO(CH ₂) ₅ R		
Nitroparaffins .. .	R.NO ₂	32.75	+890.0
Ethers .. .	R.O.R	32.20	+136.0
Ethers .. .	R.O.CH ₂ R	32.20	+128.3
Olefines .. .	R.CH=CH ₂	22.89	+13.47

The boiling-points in the preceding tables are all at 760 mm. pressure. In a further paper the writer proposes to investigate the changes which are necessary in the "constants" when the boiling-points at other pressures are considered. From a few preliminary calculations it appears that for the paraffins and fatty acids at least it is only necessary to change the "constant" *a*. *b* appears to be quite independent of the pressure.

A RAPID VOLUMETRIC METHOD FOR DETERMINING *o*-, *m*-, AND *p*-CRESOLS, THYMOL, AND PHENOL.*

By L. V. REDMAN, A. J. WEITH, and F. P. BROCK.

THIS method determines by one titration rapidly and accurately:—

- Ortho-, meta-, and para-cresols or phenol.
- The meta-cresol in the presence of *o*- and *p*-cresol.
- Phenol in the presence of *o*- and *p*-cresol.
- The meta-cresol, the phenol, and the sum of the *o*- and *p*-cresols in any mixture of these compounds.

Three methods have been proposed for determining the cresols separately:—

- Gravimetric, weighing the ortho- and para-cresol as the dibrom-cresol-bromide, the meta-cresol as tribrom-cresol-bromide (Ditz and Cedivoda, *Zeit. Angew. Chem.*, 1899, xii., 1873; Ditz and Bardach, *Biochem. Zeit.*, 1911, xxxvii., 272; Siegfried and Zimmermann, *Biochem. Zeit.*, 1910, xxix., 368).
- Volumetric, by Koppeschaar's solution, titrating back the unabsorbed bromine (Ditz and Cedivoda, *Zeit. Angew. Chem.*, 1899, xii., 1873; Ditz and Bardach, *Biochem. Zeit.*, 1911, xxxvii., 272; Siegfried and Zimmermann, *Biochem. Zeit.*, 1910, xxix., 368).
- Volumetric, by using a solution of iodine in sodium acetate and titrating back the unabsorbed iodine with thiosulphate (Pence, *Journ. Ind. Eng. Chem.*, 1912, iv., 518).

The last method does not serve for the quantitative determination of *m*-cresol.

A special method has been devised for determining *m*-cresol in the presence of ortho- and para-cresol, by weighing the *m*-cresol as trinitro-*m*-cresol (F. Raschid, *Zeit. Angew. Chem.*, 1900, xiii., 759; F. Russig and G. Fortmann, *Zeit. Angew. Chem.*, 1901, xiv., 157). The *o*- and *p*-cresol are oxidised away by strong nitric acid and trinitro-phenol is soluble if present in small amounts, *i.e.*, up to 10 per cent. The method therefore is reliable in the presence of *o* and *p*-cresol and less than 10 per cent of phenol. H. Ditz has given the following equations whereby the *m*-cresol present in a mixture consisting only of the three *o*-cresols may be determined (H. Ditz, *Zeit. Angew. Chem.*, 1900, xiii., 1050; H. Ditz and F. Bardach, *Biochem. Zeit.*, 1911, xxxvii., 272):—

$$x + y = a \quad \dots \dots \dots (1).$$

$$\frac{3\text{Br}.x + 2\text{Br}.y}{108.064} = b. \quad \dots \dots \dots (2).$$

x = meta-cresol.

y = *o*- and *p*-cresol.

a = weight of mixture of cresols taken.

b = weight of Br disappearing.

Br = 79.97 grms.

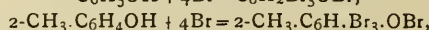
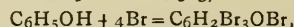
The same equations will apply to a mixture of the *o*- or *p*-cresols and phenol. The Equation 2 is modified for the formula weight of the phenol as follows (Siegfried and Zimmermann, *Biochem. Zeit.*, 1910, xxix., 368):—

$$\frac{3\text{Br}.x}{94.048} + \frac{2\text{Br}.y}{108.064} = b. \quad \dots \dots \dots (3).$$

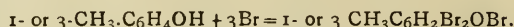
x = the amount of phenol in the mixture taken.

Siegfried and Zimmermann (*Biochem. Zeit.*, 1911, xxxvii., 272) have criticised H. Ditz and Cedivoda's method, and have shown that variable results from 2 to 20 per cent are obtained by brominating the cresols in an acid bromine solution. Their method varies from that of Koppeschaar's for determining phenol, only in the fact that one hour's time is allowed after the KI is added before the thiosulphate is run into the solution. F. Russig and G. Fortmann (*Zeit. Angew. Chem.*, 1901, xiv., 157) have also criticised Ditz and Cedivoda's method adversely. Ditz replied to their objections (*Zeit. Angew. Chem.*, 1900, xiii., 1050), and H. Ditz and F. Bardach (*Biochem. Zeit.*, 1911, xxxvii., 272) have published results at variance with Russig and Fortmann's conclusions.

Recently, Pence (*Journ. Ind. Eng. Chem.*, 1912, iv., 518) has shown that Koppeschaar's solution in an acid menstruum will determine quantitatively the meta-cresol as tribrom-meta-cresol. But the ortho- and para-cresols could not be determined either as the dibrom-cresols or the dibrom-cresol bromide, since the amount of bromine absorbed varied between the amounts required to form the dibrom-cresol and the dibrom-cresol bromide. Phenol, *o*-, *m*-, and *p*-cresols all form the bromides in the presence of excess bromine, and if the precipitates are filtered off before the KI is added the reaction is nearly quantitative, according to the following equations (Ditz and Cedivoda, *Zeit. Angew. Chem.*, 1899, xii., 1873; Autenrieth and Beuttel, *Arch. Pharm.*, 1910, ccxlviii., 112; A. Seidell, *Am. Chem. Journ.*, 1912, xlvii., 523):—



and—



The methyl group of the cresols will be slowly replaced by Br if left in contact with excess Br for several days. This has been shown by Autenrieth and Beuttel (*Archiv. der Pharm.*, 1910, ccxlviii., 112). However, if the KI be added while the precipitate is present in the acid solution the free hydriodic acid reduces the bromide as follows:—
 $\text{C}_6\text{H}_2\text{Br}_3\text{OBr} + \text{HI} = \text{C}_6\text{H}_2\text{Br}_3\text{OH} + \text{Br} + \text{I}.$ This reduction is complete for phenol (Rhodes and Redman, *Journ. Ind.*

* *Journal of Industrial and Engineering Chemistry*, v., No. 10.

Eng. Chem., 1912, iv., 655) and meta-cresol (Pence, *Eng. Ind. Eng. Chem.*, 1912, iv., 518); consequently, they may be determined accurately by adding bromide bromate to their acid solution, later adding KI and titrating back with thiosulphate. For the *o* and *p*-cresol the case is somewhat different. The hydriodic acid does not reduce the bromide completely in a reasonable length of time, and, as a consequence, all the results of the different investigators show that by this method more than 2 molecules of bromine are absorbed for each molecule of *o*- or *p*-cresol present. The authors of this paper have brominated the *o*- and *p*-cresols by the same method as described by Koppeschaar, and modified later for determining phenol (*Journ. Ind. Eng. Chem.*, 1912, iv., 655; 1913, v., 389), and the results have shown in every experiment that the bromine in the hydroxyl is gradually replaced by the hydrogen of the hydriodic acid, but the reaction is so slow that after an hour's time 6 to 40 per cent of the bromine still remains in the hydroxyl. For rapid and accurate work then, the acid bromine menstremum is not satisfactory in determining *o*- and *p*-cresols.

Recently, a method was devised by Wilkie, using a sodium bicarbonate and iodine solution for determining phenol (*Journ. Soc. Chem. Ind.*, 1911, xxx., 398). The authors of this paper have found the method quite accurate, and when modified by diluting and continuous shaking the phenol may be determined to an accuracy of two parts in a thousand with a reaction period of only one minute (Ditz and Cedivoda, *Zeit. Angew. Chem.*, 1899, xii., 1873; Autenrieth and Beuttel, *Arch. Pharm.*, 1910, ccxlviii., 112; A. Seidell, *Am. Chem. Journ.*, 1912, xlvii., 523). No subsequent filtering off of the precipitate is needed as in Wilkie's method. The short reaction period does not reduce the precipitate enough to obscure the end-point. Wilkie's method is a modification of Messenger and Vortmann's (*Ber.*, xxiii., 2753), who used caustic soda in place of sodium bicarbonate. Messenger and Vortmann's results are not very satisfactory. Gardner and Hodgson (*Journ. Chem. Soc.*, 1909, xcv., 1819) have modified Messenger and Vortmann's method so that only one iodine is absorbed by each molecule of phenol.

Pence has used an iodine solution for determining *o*- and *p*-cresol in the presence of sodium acetate (*Journ. Ind. Eng. Chem.*, 1912, iv., 518). He found that this method would work satisfactorily for *o*- and *p*-cresol but not for the meta-cresol. The present authors have found iodine in sodium acetate too slow for a reaction period of one minute. (Pence recommends one hour).

The authors of this paper have not tested the gravimetric method for determining the cresols as dibrom-*o*- and *p*-cresol bromides, and tri-brom-*m*-cresol bromide, as the gravimetric is tedious and slow in the drying of the precipitates; the precipitate gives off the odour of bromine during drying, and is at best not accurate within 1 to 2 per cent (Siegfried and Zimmermann, *Biochem. Zeit.*, 1910, xxix., 368).

Problem.—There remains, then, to discover a rapid and accurate volumetric method, which will serve equally well for the determination of each of the three cresols and phenol. If such a method can be found, it will be possible to determine by a single titration (1) the amount of *m*-cresol in a mixture of the three cresols, (2) the amount of phenol in a mixture of *o*-, *p*-cresol, and phenol, (3), the amount of phenol and meta-cresol, and the sum of the *o*- and *p*-cresols in a mixture of all four.

The Method.—Such a method has been found by determining the cresols in very dilute solution (Redman and Rhodes, *Journ. Ind. Eng. Chem.*, 1912, iv., 655), N/100, using an N/30 solution of iodine dissolved in KI (Messenger and Vortmann, *Ber.*, xxiii., 2753), adding the sodium bicarbonate (Wilkie, *Journ. Soc. Chem. Ind.*, 1911, xxx., 398), until the mixture is about half normal, shaking continuously the reacting mixture for one minute, acidifying, and titrating back the excess iodine with thiosulphate.

(To be continued).

HYPOTHEITICAL COMBINATIONS IN WATER ANALYSIS.*

By R. B. DOLE

Introduction.

THE procedures followed in determining the various mineral ingredients of natural waters have become fairly well standardised, the differences of opinion in that respect now being chiefly in regard to the accuracy with which determinations should be made. The form of reporting the result is, however, still a fruitful source of inconvenience and disagreement. The mineral constituents are variously reported in ionic form, in hypothetical combination, in oxide form, and in equivalent of calcium carbonate. This divergence of practice makes it impossible to compare the work of two chemists without definite knowledge of their methods of computation and laborious recalculation of their results. Consequently, an effort is being made to agree on a uniform manner of reporting results in connection with the formulation of standard methods for the analysis of water, now being conducted jointly by committees of the American Chemical Society, the American Public Health Association, and the Association of Official Agricultural Chemists. This paper discusses the present confusing condition and the advantages of reporting the actual facts of analysis in ionic form.

Fact versus Opinion.

A statement of an analysis in hypothetical combination is obviously a mixture of fact and opinion. The amounts of iron, calcium sulphate, and other radicles are determined by various reactions; approximate separation of scaling from non-scaling constituents is effected by treatment with dilute alcohol; but further than this, ordinary chemical tests contribute little to knowledge regarding the chemical composition of mineral waters, and consequently the exact amounts of the different salts in solution are largely conjectural. Though salts are probably present it is a mathematical impossibility correctly to apportion the bases among the acids after having found only the amounts of the acids and bases present.

Common Forms of Combination.

As this lack of definite information gives free rein to the imagination there are many opinions as to how the bases and acids should be combined. Though each method has ardent advocates, each is a personal selection whose excellence can be proved only by theory. In order to show the essential practical differences in schemes of combination and some of the confusion to which they lead, the most common methods have been applied to the analysis of the water of Missouri River shown in Table I. This chemical composition is not at all exceptional, but it has been purposely selected because it represents a large group of waters in which carbonate is sufficient to satisfy either calcium or magnesium but insufficient to satisfy both.

The first advantage of stating the actual facts of an analysis is seen by observing the reacting values or combining equivalents, which have been computed by multiplying the amount of each radicle by its valence and dividing the product by its molecular weight, for they indicate that the probable error of this analysis is about 0.3 per cent. When hypothetical combinations are made, one of three procedures is usually followed:—

1. All the bases and acids except the alkalis present in appreciable amount are estimated and the excess of acid is computed to an equivalent of sodium and potassium salts.

* Paper read before the Division of Water, Sewage, and Sanitation at the 49th Meeting of the American Chemical Society, Cincinnati, April 6-10, 1914. Published by permission of the Director, United States Geological Survey. From the *Journal of Industrial and Engineering Chemistry*, vi., No. 9.

TABLE I.—Analysis of the Water of Missouri River near Ruegg, Mo. U.S. Geol. Survey, Water-Supply Paper, cccxxvi., 80.

Results in parts per million.			
Constituents.		Results of analysis.	Reacting values.
Silica (SiO ₂)		29.0	—
Iron (Fe)		0.5	0.0179
Calcium (Ca)		52.0	2.5948
Magnesium (Mg)		16.0	1.3136
Sodium (Na)		31.0	1.3454
Potassium (K)		6.5	0.1664
Carbonate radicle (CO ₃)		0.0	0.0000
Bicarbonate radicle (HCO ₃)		178.0	2.9192
Sulphate radicle (SO ₄)		104.0	2.1632
Nitrate radicle (NO ₃)		2.9	0.0467
Chlorine (Cl)		12.0	0.3384
Dissolved solids by evaporation		346.0	—
Total reacting value of basic radicles		—	5.4381
Total reacting value of acid radicles		—	5.4675
Error of closure of reacting values (per cent)		—	0.27

TABLE II.—Hypothetical Combinations Representing One Analysis (see Table I.).

	1.	2.	3.	4.	5.	6.	7.
SiO ₂ ..	29	29	29	29	29	29	29
Fe ₂ O ₃ ..	—	—	—	0.7	—	0.7	0.7
Fe(HCO ₃) ₂ ..	1.6	1.6	1.6	—	1.6	—	—
Ca(HCO ₃) ₂ ..	210	210	36	8	126	130	210
CaSO ₄ ..	—	—	147	147	68	68	—
CaCl ₂ ..	—	—	—	19	—	—	—
Ca(NO ₃) ₂ ..	—	—	—	—	4	—	—
Mg(HCO ₃) ₂ ..	20	20	96	96	96	96	24
MgSO ₄ ..	62	62	—	—	—	—	60
NaHCO ₃ ..	—	—	94	128	—	—	—
Na ₂ SO ₄ ..	80	80	—	—	83	83	83
NaCl ..	10	13	10	—	10	20	20
NaNO ₃ ..	4	—	4	—	—	—	—
KCl ..	12	9	12	—	12	—	—
KNO ₃ ..	—	5	—	—	—	—	—
Sum. . .	429	430	430	428	430	427	427
Scale - forming constituents ..	233	233	255	257	236	235	236
Foaming constituents	106	107	80	82	105	103	103

2. All the bases and acids except carbonate are estimated and the excess of base computed to an equivalent of carbonates.

3. All the bases and acids are determined and the figures representing the salts are "doctored" to balance. These practices effectually conceal errors of technique and leave it entirely to the judgment of the analyst whether his error of closure is reasonable, and the evidence on which his judgment is based is completely masked because his hypothetical combinations show no error at all. On the other hand, the probable accuracy of the work can be calculated directly from the ionic statement as indicated in the table.

Silica has not been included among either acids or bases. Some waters (F. W. Clarke, U.S. Geol. Survey, 1911, *Bull.* cccxc., 183) of unusual character may contain the silicate radicle, but it is safe to conclude that it is absent from most natural waters. Whether silica is a colloid depends on our definition of colloid, but whatever it may be called it does not usually enter into the system of reactive bases and acids. This conclusion was reached several years ago by Kahlenberg and Lincoln (*Journ. Phys. Chem.*, 1898, ii., 77), and Kohlrausch (*Zeit. Phys. Chem.*, 1893, xii., 773) and others make practically the same statement. Among 8000 analyses of surface waters from all parts of the United States the writer finds that if silicate is not included the acid radicles are in excess in

40 per cent and the basic radicles in 60 per cent of the analyses, and that the difference either way amounts to only 1 or 2 parts per million, bears no mathematical relation to the quantity or the proportion of silica, and may as reasonably be explained by error of analysis as in any other way. This digression is inserted because it has been proposed to the committee to include rules for computing silica to silicates of the various bases.

Table II. gives hypothetical combinations of the analytical data in Table I. All the sets of combinations represent schemes used either by a large number of analysts or by one or two concerns that examine many samples from all parts of the country. The list might be much more extensive. No extreme, but mathematically correct, schemes that are unused have been introduced, and the table has been further simplified by omitting all but the more commonly-measured constituents. The only difference between Columns 1 and 2 is that sodium nitrate is calculated in one and potassium nitrate in the other. In Column 3, however, calcium is combined first with sulphate instead of carbonate. In Column 4, calcium is combined successively with sulphate, chlorine, and carbonate. Columns 6 and 7 represent methods used by certain boiler-water analysts, who ordinarily determine and report iron as the oxide and do not separate sodium and potassium but compute both together as sodium. As these analysts would not determine nitrate in a water containing so little as that under discussion absence of that radicle has necessarily been assumed. Bicarbonates instead of carbonates also have been computed because analysis shows that the carbonate radicle is absent; this slight deviation from the directed methods, however, makes no difference in the theory and permits direct comparison with other schemes. According to the scheme in Column 5 calcium nitrate, instead of potassium or sodium nitrate, is computed. According to that in Column 6 as much as possible of magnesium bicarbonate is computed first, while according to that in Column 7 as much as possible of calcium bicarbonate is computed first.

The most obvious deduction from these figures is that it is impossible to compare the report of one analyst with that of another without recalculation. The next thought that comes to most of us is that the other man's scheme is incorrect. Some would object to calculation of calcium nitrate at the expense of calcium carbonate and some to calculation of calcium chloride in the presence of sodium bicarbonate, while others would prefer to calculate magnesium sulphate instead of calcium sulphate. Aside from the theoretical merits of the methods, consideration of which would provoke endless discussion, there are these alarming facts:—

1. All are widely-used methods of reporting the analysis of one water.

2. The results cannot be directly compared with one another.

3. The results are used for estimating the quality of the water.

4. The results are given to men who, not being chemists, are incompetent properly to discount the statements, but take them at their face value.

One more digression may be permitted for the purpose of referring to the sums of the computed constituents. The sums in the last half of the table are a little lower than the others because nitrate and ferrous carbonate are disregarded. If these constituents had been computed all the sums would have been alike, the slight numerical differences among them being due to casting off decimals. Reference is made to this agreement because some chemists, no doubt thoughtlessly, consider their methods of combination correct because they "come out even." One reports that he never has any acid or base left over, or very little, and another that the sum of his calculated constituents agrees very closely with total solids by evaporation. These comments prove the excellent technique of analysis but not the chemical correctness of the combinations. Reference to the reacting values in

the first table makes it obvious that, except by error of analysis, there can be no surplus of base or acid and that the sums must agree, no matter how the radicles are combined or whether the combinations are logical.

The disagreement between Column 1, in which sodium nitrate is computed, and Column 2, in which potassium nitrate is computed, causes several embarrassing numerical differences, and the layman understands that one analyst found saltpetre where the other did not. Though this difference may be practically unimportant some similar ones might lead to serious misunderstanding. Whether the belief is well founded that lithium is a very valuable ingredient of medicinal waters need not be discussed, but if it is desired to convey an idea of the therapeutic effect of lithium the hypothetical combinations are likely to mislead those who are not aware of the limitations of water analysis. If a water contains one part per million of lithium one can compute 5.3 parts of lithium carbonate, 6.1 parts of lithium chloride, 7.9 parts of lithium sulphate, or 9.7 parts of lithium bicarbonate. If the water had the property of causing any physiologic reaction by virtue of its content of lithium it would exert that property in proportion to its content of the lithium radicle; yet by expressing that content as lithium bicarbonate instead of the carbonate the content of lithium salts has apparently been nearly doubled and in the mind of the spring owner and his clientele, for whom these compounds are computed, the therapeutic value of the analysis, if not of the water, has been doubled.

Interpretation of Results.

In the conventional methods of interpreting the various hypothetical combinations there is general agreement in some features and disagreement in others. Table II. shows the estimates of scale-forming and non-incrusting or foaming constituents that the analysts would report agree fairly well with one another, the numerical differences being too small to cause essential difference in judging the value of the water. Corresponding estimates of the amounts of soda-ash and lime to soften the water would agree as closely as the sums of the constituents, because, although each analyst computes different constituents, he cannot thereby change the amounts or relative proportions of the radicles with which the softening chemicals react. In deciding whether the water would be corrosive there is greater diversity of opinion. The analyst whose combinations are reported in Columns 3 and 6 apparently would state that the water is non-corrosive. The man whose method is shown in Column 5 would doubtless report the water to be slightly corrosive, as he computes calcium nitrate. The calcium chloride indicated in Column 4 could hardly be considered corrosive in presence of so much sodium bicarbonate. In the other three statements magnesium sulphate but not calcium sulphate is reported, and there is in them no apparent reason for stating whether the water is corrosive or non-corrosive.

Combinations Unnecessary.

Though hypothetical combinations are confusing and purely conventional many chemists assert that they are necessary in ascertaining the value of a water and in conveying a proper knowledge of the quality of the water.

As to the reported insistence by the lay public so-called on hypothetical combinations that can be understood, it is pertinent to inquire seriously how much any series of chemical figures means to the layman and whether it is not better to report the basic facts for the information of the expert and to add interpretations of the figures for the information of those who are unable to make proper deductions for themselves. Rather intimate experience for several years with lay comments on water analyses has made me extremely sceptical as to how much of the truth hypothetical combinations convey to many men who are supposed to make practical use of the results. What the manufacturer or engineer wants to know is how a particular water will fit some use to which he wishes to put it. Is it

safe to drink? Does it taste bad? Will it stain clothes? How much scale will it form in boilers? How can it be softened? Answering these questions is the function of an expert, who interprets the facts of analysis in the light of practical experience. It could be shown that hypothetical combinations are not necessary for answering these questions, though the discussion will be confined to interpretation in reference to therapeutic value and quality for boiler use.

Mineral Waters.

Waters are analysed more carefully and therefore more expensively for ascertaining their therapeutic value than for any other purpose. Mineral salts that cause definite physiologic reactions when drunk cause the reactions in relation to the radicles that are present. A solution of magnesium sulphate, for example, can be so dilute that it has no perceptible taste. An equivalent concentration of sulphate in the form of ferrous sulphate has a distinct taste, and a solution of ferric chloride containing in turn an equivalent concentration of iron has a similar taste, while again an equivalent concentration of chloride as sodium chloride has no perceptible taste. That is, in the iron solutions we taste the iron and not the sulphate or the chloride, and in order to perceive the taste of the sulphate or the chloride radicle we must use a much stronger solution of a salt whose basic radicle is comparatively weak in its effect on the organs of taste. Twenty grms. of magnesium sulphate has greater laxative action than 20 grms. of sodium sulphate, because the magnesium ion also induces laxative action, whereas the sodium ion does not, as can be shown by an equivalent dose of sodium in the form of sodium chloride. These rather crude illustrations serve to indicate that the physiologic action of a salt is caused by one or more of the radicles composing the salt and is in proportion to their concentration. The probable cathartic effect of a sulphate water can therefore be measured by its content of sulphate, computation of the possible mathematical proportions of sodium, potassium, magnesium, and calcium sulphates being unnecessary. The cathartic action of a water is increased by its content of magnesium whether it may be possible to compute the magnesium as sulphate, chloride, or bicarbonate. As for the minor constituents of mineral waters, lithium, bromide, iodide, manganese, strontium, and the like, it would not now be necessary to combat so many fallacious ideas concerning their therapeutic value if serious consideration had heretofore been given to the concentration of these radicles instead of to the possible mathematical combinations in which they might be reported.

Boiler Waters.

In a very condensed article, H. Stabler (*Engineering News*, 1908, lx., 355; also U.S. Geol. Survey, 1911, *Water-Supply Paper* 274, 165) has shown how the scale-forming constituents, the foaming constituents, the tendency toward corrosion, and the quantities of softening reagents can be computed directly from the radicles without recourse to hypothetical combinations. Though it has been objected that Stabler makes the same assumptions as are made in combining the radicles as salts, this is true only in so far as his formulæ are based on some of the currently accepted views of the reactions that occur in boilers, concerning which much is yet to be learned; and there remains the essential difference that by use of his formulæ no theoretical salts, but the estimates that are helpful to the practical man, are obtained. Comparison of the figures at the ends of the preceding tables shows that the estimate of scale directly from the radicles agrees closely with those based on combinations. All unite in including silica, iron, and aluminium as the oxides; whether there is silicate in the scale, as some have suggested, makes no arithmetical difference in the total. Magnesium carbonate and magnesium sulphate are commonly included in total scale, though magnesium is precipitated mostly as the hydrate under high-pressure

conditions and the oxide better represents what is found in the scale, as in Stabler's formula. Some prefer to compute the greatest possible amount of calcium carbonate and some the greatest possible amount of calcium sulphate; calcium doubtless is precipitated in both forms and an average between them is struck in Stabler's formula.

Similarly an average is struck among the three possible sodium salts in computing the foaming constituents by multiplying sodium by 2.7. Other conditions besides the presence of a large amount of sodium salts can cause foaming, and some believe that foaming has no relation to the concentration of the sodium salts. If, however, the interpreter of an analysis believes that the sodium salts measure the foaming tendency he gets as good estimate of that tendency by multiplying sodium by 2.7 as by computing three different salts and adding the results together.

Corrosion is considered partly a problem of reaction that involves chiefly the setting free of acids by precipitation of magnesium as the hydrate. That corrosion may be caused wholly or partly by other conditions need not concern us in discussing the practical interpretation of this theory. Stabler's formulæ provide for the three possibilities. If there is not enough carbonate to combine with all the magnesium some sulphate or chloride would be set free and the water would be corrosive; under such conditions those who compute hypothetical combinations report magnesium sulphate or magnesium chloride, the former of which is classed as corrosive by many analysts and the latter universally as corrosive. If there is enough carbonate to satisfy or more than satisfy both calcium and magnesium the water probably is non-corrosive; under such condition it is customary to compute all the calcium and magnesium as carbonates, to give the excess to sodium, and to class the water as non-corrosive. Thus far boiler-water analysts agree in so far as this theory of corrosion is accepted. If carbonate is sufficient to combine with calcium or magnesium alone but not with both, corrosion might or might not occur. The latter condition is that in the water under discussion, and the combinations in the second table show that various analysts calculate diversely magnesium sulphate, calcium sulphate, and calcium nitrate, and disagree as to whether corrosion would occur. The uncertainty of the corrosive action is quickly revealed by Stabler's formulæ without recourse to combinations. Corrosion occurs with waters that would not be classed as corrosive by any of these calculations, but that is due to other conditions, and its probability is revealed by computations of hypothetical combinations no more than by consideration of the reaction of the radicles.

Combinations not Endorsed.

Evidence of desire on the part of chemists to break away from conventional combinations of the constituents found by analysis is furnished by the resolutions adopted by various scientific organisations. As early as 1886 a committee appointed by the Chemical Society of Washington recommended (*Bull. Chem. Soc. Washington*, 1887, No. 2, 35) that all analyses of water should be stated in terms of the radicles found, whether elementary or combined, meaning evidently expression of the immediate results of the analysis; though this committee recommended that the combinations deemed most probable by the chemists making the analyses should also be reported it failed to recommend a manner of combination, and it is understood that the reason for lack of such recommendation is that the members of the committee could not agree on one convention.

The report of this committee was adopted (*CHEM. NEWS*, 1887, lvi., 113) by Section C of the American Association for the Advancement of Science in 1887, and two years later a committee of the British Association for the Advancement of Science, while agreeing with the American Association in reporting the analytical data obtained by direct determination, disapproved (*CHEM.*

NEWS, 1889, lx., 203) the statement of the mineral ingredients combined as salts unaccompanied by the original analytical data. At the Fifth International Congress of Applied Chemistry (*Ber. V. Int. Kong. Angew. Chem.*, 1903, i., 261) the discussion of two papers on methods of expressing the results of water analyses indicated that many of the chemists present favoured the ionic form of statement, and at the Sixth Congress, Christomanos (*Atti del VI. Cong. Int. di Chimica Applicata*, 1907, vii., 213) recommended that the simple statement of the acid and basic radicles in parts per million be made in all water analyses. The methods of making hypothetical combinations in early editions of Fresenius's "Quantitative Analysis" are accompanied by the statement that they are general rules for which the analyst should exercise a latitude of selection (see Second American Edition, 1896, p. 674). As Fresenius's book represents to a great extent a collective opinion it is interesting to note that a recent edition omits all rules for calculating combinations, calls attention to the effect of solubility and mass action on affinity, the impossibility of comparing the reports of two analysts, and urges statement of the direct results (Cohn's Translation of Sixth German Edition, 1904, ii., 274). A similar opinion is expressed in Tiemann-Gärtner's "Handbuch der Wässer." In this country, Handy (*Engineering News*, 1904, li., 500), McGill (*Bull. Am. Ry. Eng. and Maintenance of Way Assoc.*, 1905, vi., 612), Kimberley (*Journ. Infect. Diseases, Suppl.*, 1905, i., 157) and several other well-known analysts have called attention to the confusing state of reports of water analyses, and Clarke (U.S. Geol. Survey, 1908, *Bull.* 330, 54) has aptly characterised hypothetical combinations as "a meaningless chaos of assumptions and uncertainties."

The figures of a hypothetically-combined water analysis express only the opinion of the man who made them, and his opinion is not only different in some respects from those of his fellow analysts but is also likely to change next year. Consequently, the statement conceals analytical facts incomparable with those concealed in other hypothetical statements, and interpretation of the data of analysis is obscured by the intervention of unnecessary combinations. In view of these facts and the apparent disinclination of the organised chemical world to approve any scheme of hypothetical combination, it seems entirely advisable for American chemists not to endorse any such convention, but to recommend simple direct uncomplicated statement of the results of analysis in ionic form.

CORRESPONDENCE.

AMMONIUM MOLYBDATE.

To the Editor of the Chemical News.

SIR,—The scarcity of this reagent is such, especially since the war started, that the price has risen from 3s. 6d. to 25s. per lb., and even at the latter figure, I understand, will not long be obtainable.

In view of the fact that its use in most steel and iron works laboratories is an absolute necessity in the rapid determination of phosphorus, I should like to know if there is not an effective method of recovering the molybdenum from the "yellow precipitate" after it has been dissolved in the standard caustic potash and titrated with standard acid.—I am, &c.,

S. W. C.

September 21, 1914.

[The mineral molybdenite (molybdenum sulphide) is found in several localities in the British Isles—in Cumberland, Cornwall, and Scotland. The preparation of ammonium molybdate from the sulphide is a matter of no difficulty. Methods of recovering molybdic acid from the yellow precipitate have been given in former numbers of the *CHEMICAL NEWS*. See, for instance, vol. xlvi., p. 243.—*Ed. C.N.*]

SCIENTIFIC APPOINTMENTS AND SALARIES.

To the Editor of the Chemical News.

SIR,—I feel it to be my duty to lay before you certain facts which have come accidentally to my knowledge regarding the appointment of a lecturer in physical chemistry at an important London polytechnic. The printed information issued to applicants, of whom, fortunately, I am not one, states that the lecturer's work "in connection with Day and Evening Students" will "consist principally of Lectures and Laboratory work in Physical Chemistry to Pass and Honours B.Sc. Students," and that he "must possess an Honours University Degree." It will thus be seen that advanced teaching is contemplated, which can only be performed efficiently by a man of considerable training and ability. The successful applicant "will be required to attend for six periods (of two and a-half or three hours each) per week," i.e., for at least fifteen hours per week, and of these six periods "about three are for evening work." Further, during the ten and a-half weeks of holiday allowed per annum, this slave of science "will be required to give such assistance to the work of the Department as may be found necessary."

For this work the princely salary of £75 per annum is offered.

On the basis of these facts it is possible to consider two hypotheses as to the ideas of the Governing Body:—Firstly, that they hope to get a really suitable man for the post; secondly, that they think of appointing a raw student.

If the first hypothesis be correct I would point out that anyone who could perform adequately the duties required would probably hold a day appointment in an institution of University rank, and, indeed, this seems to be implied by the description of "Part Time Lecturer." On the other hand, it must be well known to the authorities of the polytechnic that in the great majority of colleges day appointments are for full time, and that their requirement of day attendance would exclude the holders of any such posts. Moreover, the proposed payment of £75 for a minimum of 622 hours attendance, i.e., at most 2/5d. per hour, is posterously inadequate for a trained teacher.

With regard to the second hypothesis it is only necessary to say that the policy of appointing an inexperienced man to teach Honours Students would, if pursued, bring its own retribution in the shape of a serious diminution of prestige.

In either case I wish to lodge a very serious protest against the proposal to pay at the rate of 2/5d. per hour for any "part time" teaching, were it even of elementary students, and to express the hope that no trained chemist will do such an injury to himself and his fellows as to accept the post.

I enclose my card, but will subscribe myself only,—

A UNIVERSITY TEACHER.

PRESENTS AND PARCELS FOR THE TROOPS.

To the Editor of the Chemical News.

SIR,—In the autumn of 1899, at the commencement of the war in South Africa, we made an offer through the Press to convey free of charge parcels of clothing, necessities, and comforts to the soldiers on active service, from their relatives and friends at home. As a result of this offer several thousand packages were received and forwarded by us.

Being desirous, if possible, of rendering similar assistance during the present war, we recently communicated with the War Office on the subject, and are now advised by the Army Council that there is plenty of scope for us to do similar service in connection with the present campaign, and that they think it would be advantageous to make this known through the medium of the Press.

Packages weighing less than 11 lbs. will not be accepted by the Military Authorities, and must be forwarded by

Parcels Post and paid for at the usual rates, but in order that soldiers' friends and relatives may receive the benefit of free conveyance we have arranged to receive packages of any weight up to 56 lbs.

We will see they are properly addressed, packed, and forwarded, free of charge, and shall be glad if you will kindly make this known through the courtesy of your columns.

According to the War Office Regulations no wines, spirits, or matches can be received, nor fresh fruit, vegetables, or any article of a perishable nature which is likely to cause damage.

Full particulars and labels may be had on application at either of the under-mentioned addresses.—We are, &c.,

NEALE and WILKINSON, LTD.,
Foreign Forwarding Agents.

32, St. Mary Axe, London, E.C.,
60, Hanover Street, Liverpool.
September 23, 1914.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxx., No. 2, July 13, 1914.

Reduction of Oxides of Copper, Lead, and Nickel.

—Paul Sabatier and Léo Espil.—The reduction of cupric oxide, CuO, by means of hydrogen leads directly to the metal, without intermediate formation of a suboxide, such as cuprous oxide. Lead oxide, PbO, between 190° and 250° gives a stable suboxide, Pb₂O, irreducible under ordinary pressure in this interval of temperatures. Nickel oxide, NiO, gives a suboxide which is reducible even at the lowest temperatures of reduction, and hence in all cases a mixture is obtained of suboxide and metal.

Oxide of Propylenedimethylacetophenone and some of its Derivatives. New Method of preparing γ -Ketonic Acids.—A. Haller and Mme. Ramart-Lucas.—When chromic acid in acetic solution acts on the oxide of propylenedimethylacetophenone the product is 3-benzoyl-3-methylbutanoic acid. The ethyl ether of the same acid is obtained by the action of brom- or iodoacetic ethers on sodium isopropylphenyl ketone. This reaction can be generalised, and provides a means of preparing a series of γ -ketonic acids, mono- or di-substituted. When phenyl magnesium bromide acts on the oxide of propylenedimethylacetophenone a compound of formula C₁₉H₂₂O₂ is obtained. The authors have prepared its oxidation products and its acetyl derivative and phenylurethane.

Ketisoketimines.—Charles Moureu and Georges Mignonnac.—Ketimines in which the carbon of the group

$\begin{array}{c} \text{—C—} \\ | \\ \text{NH} \end{array}$ is united to an atom of carbon combined with

hydrogen, when heated give rise to ketisoketimines by condensation of two molecules with loss of ammonia. These ketisoketimines are yellowish green oils, thick and very viscous, and smelling faintly. With dilute hydrochloric acid they give ammonia and the corresponding ketone. They give up no gas when treated with ethyl magnesium bromide, and hence no hydrogen is combined with the nitrogen.

Glucinum Sulphate and its Hydrates.—F. Taboury.—The progressive dehydration of SO₄Gl_{1.4}H₂O confirms the existence of the hydrates containing one and two molecules of water, and appears to indicate that of a hydrate containing 0.5H₂O. The partial dehydration at the ordinary temperature of solutions of the hydrate containing 4H₂O, by means of H₂SO₄, yields SO₄Gl_{1.2}H₂O.

The stability of SO_4Gl up to $530\text{--}540^\circ$ enables glucinum to be determined as sulphate. SO_4Gl does not seem to form acid sulphates. This differentiates glucinum from the other metals of the same family.

Penot's Chlorometric Method.—J. Clarens.—By Penot's method the amount of hypochlorite in a solution is determined by the quantity of sodium arsenite which it can oxidise. The oxidation is known to be complete when a drop of the liquid no longer colours iodide and starch-paper. In Mohr's modification the sample of hypochlorite is treated with an excess of arsenious liquid which is determined by means of a titrated solution of iodine. The author has investigated the accuracy of the two methods. He finds that Penot's method is sufficiently accurate for commercial purposes, but is less accurate and gives lower results than Mohr's modification. It is best to add a small quantity of potassium bromide to the liquid instead of using iodide and starch-paper.

Method of preparing Complex Compounds of Divalent Platinum.—L. Tschugaeff.—The chloroplatinite of tripropylammonium, $[\text{N}(\text{C}_3\text{H}_7)_3\text{H}]_2\text{PtCl}_4$, in chloroform solution can be used to prepare complex platinum compounds. Thus with methylcarbylamine it gives $[\text{Pt}(\text{CH}_3\text{NC})_2]\text{PtCl}_4$. With hydrazine new hydrazino platinum compounds are obtained, and the same chloroplatinite can be used to prepare the compounds which platinum chloride forms with aromatic phosphines, arsines, and stibines.

Hydrogenation of Compounds containing Ethylenic Bonds in presence of Nickel.—André Brochet and Maurice Bauer.—The hydrogenation of compounds containing ethylenic bonds takes place very readily in presence of nickel under moderate pressure. Free or combined cinnamic acid very rapidly undergoes hydrogenation, while piperonylacrylic acid is hydrogenated less easily. Cyclic compounds with an allylic or propenylic side-chain react similarly.

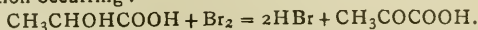
Atti della Reale Accademia dei Lincei.

Vol. xxiii., [i.], No. 10, 1914.

Phenomena of Transformation of Molybdates and Tungstates.—M. Amadori.—Sodium molybdate is tetramorphic, having points of transformation at 634° , 592° , and 444° . The tungstate is trimorphic, the points of transformation obtained on cooling being at 582° and 571° . The corresponding potassium salts are both trimorphic, the transformation temperatures being respectively:— 460° , $322\text{--}326^\circ$; 600° , $370\text{--}374^\circ$.

Position of Cerium in the Periodic Table and the Complex Molybdates of Tetravalent Cerium.—G. A. Barbieri.—If cerium is a member of the fourth group of the Periodic Table and, in particular, if it occupies a position between zirconium and thorium, it is logical to suppose that it will give complex molybdates analogous to those of the homologous elements. This is confirmed by experiment, and the author has obtained the compound $4(\text{NH}_4)_2\text{O} \cdot \text{CeO}_2 \cdot 12\text{MoO}_3 \cdot 8\text{H}_2\text{O}$ corresponding to the neutral thoromolybdate of ammonia. The cerium, like the thorium compound, crystallises in prisms insoluble in water but soluble in dilute acids. The acid solution when treated with an ammonium salt gives a precipitate of the compound $3(\text{NH}_4)_2\text{O} \cdot \text{CeO}_2 \cdot 12\text{MoO}_3 \cdot 11\text{H}_2\text{O}$, differing by 1 molecule of water from the corresponding thorium compound. Ceric-molybdic acid is octobasic, as is proved by the existence of the silver salt $4\text{Ag}_2\text{O} \cdot \text{CeO}_2 \cdot 12\text{MoO}_3$.

Oxidations with Bromine under the Action of Light.—R. Ciusa and A. Piergallini.—When a solution of lactic acid in bromine water is exposed to the action of light for a day pyruvic acid is formed, the following reaction occurring:—



Tartaric acid in the same circumstances gives formylglyoxylic acid and carbon dioxide. Glycerin is oxidised to glycerose, and citric acid yields pentabrom acetone.

MISCELLANEOUS.

Alchemical Society.—The next General Meeting will be held at 1, Piccadilly Place, W., on Friday, October 9, at 8.15 p.m., when a Presidential Address will be delivered by Prof. John Ferguson, M.A., LL.D., &c., on the works of George Starkey. Visitors are invited.

Canada's Gift.—Sacks to be Sold at 5s. each.—Canada is making a splendid gift of flour to the Mother Country. It has been decided that the sacks, when empty, should be sold as souvenirs at 5s. each. Two-thirds of this sum will be devoted to the Prince of Wales's National Relief Fund and one-third to the Belgian Refugees Fund. The sacks are all marked "Canada's Gift." Applications for the sacks as souvenirs, accompanied by a remittance of 5s., should be sent to the Hon. Secretaries, National Relief Fund, York House, St. James's Palace, London, S.W. Applications will be dealt with in strict rotation.

Supply of Laboratory Reagents and Glass Apparatus.—At a Joint Meeting of the Councils of the Institute of Chemistry and the Society of Public Analysts held recently, Committees were appointed—

(a) To consider what steps shall be taken to ensure a continued satisfactory supply of laboratory reagents.

(b) To consider what steps shall be taken to insure a continued satisfactory supply of glass apparatus.

Both Committees are empowered to co-opt additional members. They are engaged in obtaining all the information they can with reference to the matters referred to them, and will report to the Councils and also to the Committee of the Board of Trade in due course.

NOTES AND QUERIES.

Tin Salts.—We have an enquiry from abroad for salts of tin (crystallised perchloride of tin), which our clients have hitherto bought in Germany. We should esteem it a great favour if you could give us the names of manufacturers in England of this product, which is used in connection with the manufacture of pins.—RILEY and WILLIE.

Synthetic Sugar.—I understand that a process has recently been invented by Mr. A. Voltaire Boyes for the synthesis of sugar on a commercial scale, and that a company is in process of formation, under the title of The Synthetic Sugar Syndicate, for the working of same. As I am anxious for further particulars, I should be glad if any reader could provide me with the address of the inventor, or of any of the promoters of the company.—SUCROSE.

DEPARTMENT OF AGRICULTURE AND TECHNICAL INSTRUCTION.

ROYAL COLLEGE OF SCIENCE FOR IRELAND, DUBLIN.

The College opens for the SESSION 1914-15 on
OCTOBER 6th, 1914.

A complete COURSE of INSTRUCTION is
given in—

AGRICULTURE and ALLIED SUBJECTS
(including Horticulture, Forestry, and Creamery Management).
CHEMISTRY, ENGINEERING, PHYSICS, & NATURAL SCIENCE.

In the Faculty of Applied Chemistry the Curriculum embraces a full course of Elementary and Advanced Inorganic, Organic, and Physical Chemistry, Chemical Technology, and Assaying, for all of which there is ample Laboratory accommodation and complete up-to-date equipment and apparatus.

Special facilities are afforded advanced students for carrying out Research investigations.

A limited number of Scholarships are offered each year—

- (a) In AGRICULTURE and ALLIED SUBJECTS.
- (b) In SCIENCE and TECHNOLOGY.

Full particulars of the conditions of entrance by examination or other qualification, of the examinations for the above Scholarships, and of the various Courses of Instruction, Fees, &c., are contained in the College Programme, which may be obtained on application to THE REGISTRAR, Royal College of Science for Ireland, Dublin.

THE CHEMICAL NEWS.

VOL. CX., No. 2863.

THE PREPARATION OF POTASH FROM FELSPAR AND OTHER SOURCES.

IN consequence of the complete stoppage of the importation of potassium salts from Germany new sources of the metal must be speedily found, and it may be of interest to call attention to a process for obtaining it from felspar, which was originally worked out and patented as long ago as 1857 (Ward, F. O., and Wynants, F., Patent No. 3185, Dec. 30th, 1857), and which, when tested upon a large scale, was found to give thoroughly satisfactory results. This process was called by its discoverer, Mr. F. O. Ward, the "calcifluoric attack of the primitive alkaliferous rocks," and was based upon earlier but unsuccessful methods, which will be briefly outlined before the process itself is described. In 1830 Sprengel prepared alum from felspar by powdering the rock finely, mixing it to a paste with concentrated sulphuric acid, and leaving the mass for several months. Extraction with water then gave a solution of pure potash alum. Some years later Turner also obtained alum from felspar, using a more complicated process, while Kuhlmann found that felspar is attacked by calcium chloride at a high temperature, potassium chloride being formed. In 1857 Meyer discovered a method of extracting potash from potassic rocks, by means of which a very pure product could be obtained. He calcined lime and felspar together at a temperature between bright red and white heat, and submitted the mixture to the action of water at a high temperature and a pressure of seven to eight atmospheres. The water then became sufficiently alkaline to exclude lime from solution, and considerable quantities of potash could thus be extracted as hydrate, or could be carbonated by the furnace gas. The difficulty and cost of lixiviating large quantities of material at a comparatively high pressure and of calcining the original mixture, precluded the possibility of this process being commercially successful.

In Ward's method, which he worked out in conjunction with Captain Wynants, the substance employed for liberating the potash contained in felspar was fluorine, in the form of fluorspar or other fluoride, and by means of it the whole of the potash in an ordinary felspar (upwards of 13 per cent) could be liberated in the caustic state, containing as impurities only a little silica and alumina. The felspar to be treated was ground to the fineness of ordinary Portland cement and mixed with powdered fluorspar or other fluoride, the amount of fluorine employed being exactly equivalent to the alkali in the rock. Chalk, or preferably a mixture of chalk and lime, was then incorporated with the mixture, in the proportion of double the quantity of lime equivalent to the silica and one and a half times that equivalent to the aluminium. In working on a large scale it was found advisable to increase the theoretical quantity of lime by one-ninth or one-tenth, for a deficiency of lime produces poor results, while a slight excess does no harm. The addition of chalk served to make the frit porous, and therefore easy to lixivate, owing to the carbon dioxide evolved on ignition, and also by fusing it brought the reacting molecules into contact with one another. The mixture was then made into balls or cakes, and heated to a yellowish-red heat, when a porous frit was obtained within a short time (from one to several hours). This was boiled or lixiviated with hot water, which dissolved all the alkali, and a solution was thus obtained containing the alkali more or less carbonated, and also some silica or alumina,

or both. The addition of lime to the liquor allowed of the separation of pure alkali. The residue might be employed after calcination as an hydraulic cement, although the presence of fluorine in it was deleterious. This might be expelled by calcining in an atmosphere or current of steam, when it would pass off as hydrofluoric or hydrofluosilic acid. On a large scale (using ordinary gas-retort charges) it was found that by this process nine-tenths of the potassium present in the felspathic rocks could be readily extracted, and, moreover, it was obtained in the most convenient and valuable form—as caustic potash or potassium carbonate. In a report of the Jury of the International Exhibition of 1862, the Reporter, Professor A. W. Hofmann, expressed his high appreciation of the process, which he believed would prove to be "the true and definitive solution of the great potash problem."

The residues of the manufacture of beet sugar may also be a valuable source of potash. The latter accumulates, if sugar is manufactured, in the molasses, which may be fermented, the spirit being distilled off, while the acid residue is treated for the extraction of potash. If the whole of the sugar in the root is converted into alcohol the potash concentrates at once in the acid residue—the vinasse. This is neutralised by the addition of chalk, and the clear liquid is separated off and evaporated, and finally calcined, until a hard, light grey, stony mass is obtained. It is essential that the calcination should proceed to and stop at exactly the right point, which requires some skill and experience on the part of the operator. The properly calcined mass should dissolve in water to give a clear, colourless solution. The crude salt thus obtained may contain 50 per cent or more of potash salts, which may be purified by fractional lixiviation and evaporation. The cultivation of the beetroot for the extraction of sugar has been proved to be practicable in the United Kingdom, where the soil and climate are generally favourable to its growth, and it has been shown on the Continent that the culture of the root and the routine work of the manufacture of sugar can readily be entrusted to the average labourer under the supervision of a few skilled men. It is, of course, obvious that the source of the potash in beetroot salts is the soil, to which potash must be returned in the form of manure. Hence this source can properly be regarded merely as providing an additional supply to meet an increased demand, while the need of potash for glass making, gunpowder, medicinal purposes, &c., remains practically unaffected by it.

The extraction of potash from sea-water, either directly or by evaporation, and the subsequent separation of the mixture of salts obtained, or indirectly by the incineration of seaweed, has been successfully performed in the past, and the revival of the kelp industry would seem to be by no means impracticable, and, moreover, it has the advantage of furnishing iodine as well as potassium.

While efforts are being made on all sides to increase the supplies of potash, it will be well also to economise in the use of it as much as possible, by employing the corresponding sodium salts, for example. The shortage in the supply of glass from abroad must ultimately be met by increased manufacture in this country, but in the meanwhile quartz glass may be substituted for ordinary glass, particularly in laboratory work. In order to make quartz glass more generally useful its fusing point must be lowered, so that it can be worked without the help of the oxyhydrogen blowpipe. This has already been effected by the addition of potassium titanate, the process being carried out by a German firm, and further experimental work will no doubt lead to the discovery of other substances having the same effect. The Silica Syndicate, Limited, of Hatton Garden, recognising the need for prompt action, have, with a great display of public spirit, considerably reduced their prices for basins, crucibles, flasks, beakers, &c., and have issued a list of temporary special prices, which leave only a very small margin of profit to the makers, but will undoubtedly lead to an increase in the use of the ware in analytical and general laboratory work.

CHEMISTS AND THE GAS MANTLE SHORTAGE.

HOW THEY MAY SOLVE THE DIFFICULTY.

THE prospect of a serious shortage in the supply of gas mantles, which hitherto have been largely manufactured in Germany, has resulted in a substantial increase in price, and is occasioning considerable consternation among those primarily interested. So grave has the position become owing to the war that in some quarters it is declared that in two or three months there is the possibility of the industry coming to a stop and no more mantles being made. There is good reason for believing, however, that those directly associated with the manufacture of this most useful and valuable adjunct of illumination are giving grave consideration to the untoward position that has arisen, and the not distant future will possibly see an extension of the gas mantle manufacturing industry in this country.

In such an extension it is obvious that chemists in the United Kingdom must fill a very important part, and, in fact, largely save the situation by entering upon a branch of specialised work which none of them apparently have ever before attempted. That work would consist of extracting from monazite sand the precious thorium and cerium to which the incandescent mantle owes its brilliance in the proportion of 99 parts of thorium to 1 of cerium. It is realised that the chief difficulty will lie in securing the requisite supplies of thorium and cerium. The best mine of monazite sand is said to be at Travancore, in India, and there are also deposits in Carolina, U.S.A., but the greater portion of the world's supply, amounting to thousands of tons in a year, comes from a mean little village on the shores of Brazil. The sand, which is worth about £80 a ton, requires many months' treatment before it is converted into a white pure nitrate of great purity which is rapidly merged into the complete mantle.

All the deposits of monazite sand appear to be controlled by a ring of German houses, situated for the main in Hamburg. The firms in England who manufacture mantles can only draw their supplies of thorium and cerium from this German ring, who, with characteristic jealousy, have always limited the amount sent here in order to prevent the accumulation of large stocks. It seems that certain American firms have some control over the Carolina deposits, but it is questionable whether they can spare any of this valuable substance.

A London gentleman, who is prominently identified with the gas mantle industry, was asked this week how he thought the scarcity of thorium in this country would be met.

"Personally," he replied, "I think there will be some arrangement made with the India Office to get it direct from Travancore, but the question then is to convert it into nitrate for use in the mantle. I don't think this has ever been done in England; it has always been done in Germany. That is for the want of chemists, I suppose, in our own country. Still, they have got to do it; there is no doubt about that."

A gentleman in a provincial city, who is also well known in the industry, when asked for his views on the subject, remarked:—"Unless other deposits of monazite sand are to be found, as well as chemists in this country to extract thorium and cerium, the industry will come to a stop, and it is estimated that in two or three months no more mantles will be made."

It has been estimated that about 400,000,000 mantles are used every year in Great Britain. This estimate, which comes from a responsible quarter, is in striking contrast with many of the estimates advanced, some of which have placed the annual consumption at 20,000,000. There is no doubt that the great bulk of the trade has been done by Germany at prices with which it has been impossible for English manufacturers to compete.

It is generally recognised that the imported mantles from Germany have been of the inferior kind—cheap

and shoddy. Those which have been manufactured in this country have been of a better quality, and in this connection it is interesting to observe that the Welsbach Company make all their own mantles at their factory in Wandsworth. With the Gas Light and Coke Company and other large lighting concerns the Welsbach Company would probably be the prime movers in an extension of the industry in this country.

A RAPID VOLUMETRIC METHOD FOR DETERMINING *o*-, *m*-, AND *p*-CRESOLS THYMOL, AND PHENOL.*

By L. V. REDMAN, A. J. WEITH, and F. P. BROCK.

(Concluded from p. 169).

Experimental.

Apparatus.—The only appliances needed are—(1) standardised burettes, (2) ground stoppered half litre bottles, (3) 25 and 50 cc. pipettes, and a shaking machine. The authors found that continuous shaking by hand of the bottles was as convenient as using the shaking machine when the "reaction period" was of only one minute's duration.

Solutions.—The solutions consisted of N/30 iodine solutions containing 1/60 formula weight of each of the three cresols and phenol, N/10 thiosulphate, N sodium bicarbonate, 2N sulphuric acid. The N/30 iodine was made up by dissolving 4.2 grms. of re-sublimed iodine in a saturated solution of 15 grms. KI, and making up to 1 litre. The standardisation of the iodine solution was by arsenious acid. The thiosulphate solution was prepared by dissolving 125 grms. of sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, in 5 litres of water, allowing the solution to stand for one week, and then standardising it against the iodine.

The three cresol solutions were made up in each case by taking 1.801 grms. of re distilled cresol, and making it up to 1 litre. The cresols were from "Merck's highest purity," and were weighed out very carefully after re-distilling.

Care was taken to exclude moisture, and the samples were weighed out and made up accurately to volume. The N sodium bicarbonate solution was made by dissolving 84.1 grms. of NaHCO_3 in 1 litre of water, the 2N sulphuric acid by adding 56 cc. of concentrated bottle acid (sp. gr. 1.84) to about half litre distilled water, and making the total volume up to 1 litre. The two latter solutions need be only approximate.

Brominating the Cresols.—At the beginning of the research a bromide-bromate solution was used, and acid added as in determining phenol. The bromination method was found to work quite satisfactorily for phenol and meta-cresol, but the amount of bromine absorbed by the *o*- and *p*-cresol at the end of the thiosulphate titration depends upon three factors.

1. The excess of free bromine present.
2. The length of time the bromine has acted upon the cresol solution.
3. The time allowed for the hydriodic acid to act upon the brominated product, reducing the dibrom-cresol bromide to the dibrom-cresol.

If enough bromine be added the reaction is complete and dibrom-cresol bromide is formed, and may be weighed as such (Ditz and Cedivoda, *Zeit. Angew. Chem.*, 1899, xii., 1873). But if the reaction in the presence of excess bromine proceeds for only one minute, the reaction is not complete. After allowing the hydriodic acid to reduce it for one minute and titrating back the excess iodine, 6 to 10 per cent of the hydroxyl still remains filled by bromine, giving an error in the determination of 3 to 5 per cent. The longer the hydriodic acid acts upon the product, the

less bromine is left in the hydroxyl until after one hour's time the reduction has proceeded within 4 per cent of completion. The difficulty seems to be one of delayed diffusion. The precipitate, which is at first flocculent and fills the whole solution, condenses into a few small solid wax-like particles which do not allow the hydriodic acid free access to the unreduced bromide. The precipitate which originally occupied a space of quarter of a litre shrinks (with partial solution) to a volume of less than 1 cb. mm., and when the colourless point is reached with the thiosulphate, one can see a continuous column of blue rising from the little granules at the bottom of the liquid, showing that the hydriodic acid is reducing (but very slowly) the dibrom-cresol bromide. Siegfried and Zimmermann tried to hasten the reduction by warming the solution, but their attempts were unsuccessful (*Biochem. Zeit.*, 1910, xxix., 368). They recommend diluting the solution to 0.025 N and allowing fifteen minutes for the "reaction period" without continuous shaking, then adding the KI, thoroughly shaking, and titrating with thiosulphate. Their results show that the cresols may be determined by this method within 1 to 3 per cent. Our experiments confirmed their results. One difference was observed; if the shaking was continuous, the precipitate decreased in volume as described above, and the determination was not accurate.

The bromine-acid method was abandoned in favour of the alkaline iodine method as the results are too dependent upon the dexterity and patience of the individual experimenters. Time was also a factor. The bromine method could not be hastened by shaking as in the case of phenol and meta-cresol, for the precipitates of dibrom *o*- and *p*-cresol bromide coagulated into such small dimensions that rapid diffusion through it of the hydriodic acid was quite impossible. Allowing a reaction period of fifteen minutes and a reduction period for the bromide of one hour after the KI is added, the method requires about one and one-half hours for determinations which are accurate only to 1 to 3 per cent. When this method is applied to a mixture of phenol and *a*- or *p*-cresol the error is aggravated and amounts to 3 to 21 per cent, according to Siegfried and Zimmermann (*Biochem. Zeit.*, 1910, xxix., 387).

Determination of *o*-, *m*-, and *p*-Cresols Separately.

Each of the cresols was determined separately, according to the following method:—About 50 cc. N sodium bicarbonate was poured into a half-litre ground stoppered bottle, 100 cc. of water added, 15 or 20 cc. of the N/10 cresol were then run in from a standardised burette, and the volume was very carefully read. Enough N/30 iodine (40—70 cc.) to colour the solution a permanent alkaline iodine colour was then added. A reaction period of one minute was allowed, during which time the solution was shaken continuously, by hand or in the machine. Then 50 cc. 2/N sulphuric acid were added, and after shaking thoroughly the excess iodine was titrated back with thiosulphate.

Tables I., II., and III. show the results for the three cresols.

Experiments 1 and 2 show that 20 per cent excess iodine and ten minutes' "reaction period" do not increase the absorption of iodine over the one minute's reaction and 14 per cent excess free iodine in Experiment 9.

Experiments 3 and 6 show that an increase of sodium bicarbonate from 1/6 N to normal does not increase the iodine absorption.

Sodium acetate was substituted for sodium bicarbonate in Experiments 7 and 8, which confirm Pence's (*Journ. Ind. Eng. Chem.*, 1912, iv., 518) results that the *m*-cresol does not go over completely to tribrom-*m*-cresol in a short time in the presence of sodium acetate.

Experiments 10 and 11 show that the results are not affected by increasing the excess of free iodine from 11 to 22 per cent and Experiments 12, 13, and 14 show the absorption to be complete in one minute's time.

TABLE I.—Determination of Meta-Cresol.

Exp. No.	NaHCO ₃ Water.	N/10 <i>m</i> -cresol.	N/30 iodine.	Reaction period.	2/N acid added.	Thio.	<i>m</i> -Cresol found.
	Cc.	Cc.	Cc.	Mins.	Cc.	Cc.	Per cent.
1.	20	100	20.00	70	10	25	4.20 100.0
2.	20	100	20.00	70	10	25	4.20 100.0
3.	20	100	15.00	50	10	25	2.26 100.0
4.	30	100	14.97	50	5	20	2.26 99.9
5.	50	50	15.02	50	5	30	2.20 100.0
6.	100	—	15.00	50	5	30	2.25 99.8
7.	(a)	—	15.00	50	5	15	3.20 93.4
8.	(a)	—	15.00	50	5	55	3.30 92.7
9.	50	100	15.00	50	1	30	2.20 100.2

(a) 100 cc N sodium acetate were added in place of the bicarbonate.

For solutions, &c., see Table III.

TABLE II.—Determination of Ortho-Cresol.

Exp. No.	NaHCO ₃ Water.	N/10 <i>o</i> -cresol.	N/30 iodine.	Reaction period.	2/N acid added.	Thio.	<i>o</i> -Cresol found.
	Cc.	Cc.	Cc.	Mins.	Cc.	Cc.	Per cent.
10.	100	—	15.00	35.0	5	55	1.70 100.0
11.	50	50	15.00	39.9	5	30	3.37 99.96
12.	50	50	20.03	50.0	1	30	3.33 99.60
13.	50	50	20.00	50.0	1	30	3.41 99.90
14.	50	50	15.00	40.0	1	30	3.14 100.30

For solutions, &c., see Table III.

TABLE III.—Determination of Para-Cresol.

Exp. No.	NaHCO ₃ Water.	N/10 <i>p</i> -cresol.	N/30 iodine.	Reaction period.	2/N acid added.	Thio.	<i>p</i> -Cresol found.
	Cc.	Cc.	Cc.	Mins.	Cc.	Cc.	Per cent.
15.	50	50	20.00	50.3	1	30	3.55 99.7
16.	50	50	15.00	50.0	1	30	6.80 100.0
17.	50	50	15.00	40.0	1	30	3.29 100.0
18.	50	50	15.00	40.0	1	30	3.22 100.0

Thiosulphate = 0.0982/N.

Sulphuric acid = 2/N.

NaHCO₃ = N.

Iodine = 0.0340/N.

Temperature = 23° C.

Experiments 15, 16, 17, and 18 show that uniform results are obtained by making the solution 1/2 N with sodium bicarbonate, allowing only one minute for the "reaction period." Excess of iodine (50 per cent in Experiment 16) did not increase the iodine absorption. It was consequently considered unnecessary to determine the effects of increased "reaction period."

It may be mentioned that the tri-iodo-meta- and di-iodo-para-cresols are precipitated as white flocculent masses before the solution is acidified. The di-iodo-ortho-cresol is precipitated as a red, more or less granular substance. On the other hand, the di-iodo-phenol is not precipitated in N/2 sodium bicarbonate and the precipitate forms only on the addition of the acid. In N/10 sodium bicarbonate the precipitate forms and is not so red as the precipitate from the stronger carbonate solution.

TABLE IV.—Determination of Phenol by Iodine-Sodium Bicarbonate Solution

Exp. No.	NaHCO ₃ Water.	Phenol solution.	Iodine.	Reaction period.	2/N acid added.	Thio.	Phenol found.
	Cc.	Cc.	Cc.	Mins.	Cc.	Cc.	Per cent.
19.	10	90	15	50	1	20	5.00 85.5
20.	10	90	15	50	1	25	3.70 94.9
21.	10	90	15	50	15	25	3.20 98.6
22.	25	75	15	50	1	25	3.00 100.0
23.	50	50	15	50	1	30	3.00 100.0
24.	50	50	15	50	1	30	3.00 100.0
25.	50	50	15	50	25	25	3.05 99.7
26.	50	50	10	50	25		

Iodine sol. = 0.03306 N. Others as in Table III.

Table IV. gives the determination of phenol by the same method as used for determining the cresols. The method does not vary from Wilkie's, except that the concentrations of the reagents are so chosen that with continuous shaking for one minute the reaction is complete. This rapid reaction leaves the precipitate a flocculent, white or pinkish mass and does not obscure the iodine-

TABLE V.—*Determination of Mixtures of o-, m-, and p-Cresols.*

Expt. No.	NaHCO ₃ . Cc.	Water. Cc.	Cresol mixtures. Cc.	Iodine. Cc.	Reaction period. Mins.	2/N acid added. Cc.	Thiosulphate. Cc.	N/10 iodine absorbed. Cc.	Calculated iodine absorption. Cc.
27.	25	75	15	40	1	25	1'5	11'75	11'73
28.	25	75	15	40	1	25	1'5	11'75	11'73
29.	25	75	14	40	1	25	2'3	10'97	10'95

For solutions, &c., see Table VI.

TABLE VI.—*Determination of Mixtures of Phenol, Ortho-, Meta-, and Para-Cresol.*

30.	25	75	20	60'0	1	25	4'02	15'88	15'99
31.	25	75	20	60'0	1	25	3'83	16'08	15'99
32.	25	75	20	60'0	1	25	3'95	15'96	15'99

Thiosulphate = 0'0982 N.
Iodine = 0'03306 N.Sulphuric acid = 2 N.
Sodium bicarbonate = N.

Temperature = 23° C.

TABLE VII.—*Determination of Thymol.*

Expt. No.	H ₂ O. Cc.	NaHCO ₃ . Cc.	Thymol. Cc.	Iodine. Cc.	Reaction period. Mins.	H ₂ SO ₄ . Cc.	20 per cent KI. Cc.	Thiosulphate. Cc.	Thymol found. Per cent.
33.	100	25	15	27'4	2	25	—	1'72	100'0
34.	100	25	10	18'0	1	25	—	1'07	100'0
35.	100	25	5	32'25	1	25	—	7'79	122'6
36.	100	25	15	32'0	1	25	—	3'20	100'8
								3'30 (a)	99'6
37.	100	25	15	30'0	1	25	5	2'58	100'2

Iodine = 0'03306/N.
Sodium bicarbonate = N.Sulphuric acid = 2/N.
Thymol = 0'0491/N.Thiosulphate = 0'0982/N.
Temperature = 23° C.

(a) This result was obtained by titrating the blue colour, which returned after the first titration. The time allowed for the blue to return was ten minutes. The blue did not return in one half-hour after the second titration.

starch colour, requiring thereby no filtering off of the precipitate as in Wilkie's method, which allows ten minutes for the "reaction period," and as a consequence a filtering off of the dark red precipitate is required. In Experiment 26, the twenty-five minutes' shaking had made the precipitate so dark that the determination could not be made without filtering.

Experiments 19 and 20 show that N/10 sodium bicarbonate is not sufficient to complete the reaction in one minute. Fifteen minutes are required for its completion under these conditions (Expt. 21). Sodium bicarbonate N/4 was used in Expt. 22, and was found to be sufficient with one minute's reaction period. One minute is sufficient time to complete the reaction with N/2 bicarbonate, and when twenty-five minutes was allowed for the reaction no further absorption of iodine took place. The precipitate was a lilac-pink. With less phenol and the same amount of iodine (Experiment 26); the precipitate was a dark wine colour and obscured the end-point in titrating back with thiosulphate for excess iodine. A precipitate appeared in Experiments 19 to 21, but no precipitate formed in Experiments 23 to 26 until the acid was added.

Determination of a Mixture of o-, m-, and p-Cresol.

A solution was made up by taking one-third by weight of each of the cresols and diluting until the strength of the solution contained (108'064/60) grms. cresols per litre. The results are given in Table V. In the second last column is given the amount of iodine absorbed by the cresols and the last column represents the amount of iodine which should have been absorbed, calculated for the amount of cresols in the solution (reckoning the ortho- and para-cresols as di-iodo-cresols and the meta-cresol as the tri-iodo-cresol). The error in each case is 0'2 per cent and reckoned as an error for any one of the three cresols represents a loss of 0'6 per cent, since they are each present in equal amounts, or if the error be distributed over each of the three ingredients, it is an error in each of 0'2 per cent.

A Mixture of Phenol, o-, m-, and p-Cresol.

The equation of Ditz to determine the amounts of m-cresol in the presence of o- or p-cresol, and modified later by Siegfried and Zimmermann for determining phenol in the presence of p-cresol, may be extended to include the determination of phenol, o-, m-, and p-cresol in the presence of all four compounds and with these equations, if there be known (1) the weight of the mixture present; (2) the total amount of iodine absorbed; the following determinations may be made from a single titration:—

1. The meta-cresol present.
2. The phenol present.
3. The sum of the o- and p-cresols present.

If x = weight of (phenol + m cresol). y = weight of (o- and p-cresol). m = Total weight taken of the mixture. e = effective formula weight of phenol and m-cresol. a = weight of phenol present. b = amount of m-cresol. n = number of mols. of iodine disappearing.

Then

$$x + y = m \quad \dots \quad (1).$$

$$\frac{3x}{e} + \frac{2y}{108'064} = \frac{n}{2} \quad \dots \quad (2).$$

$$a + b = x \quad \dots \quad (3).$$

$$\frac{a}{94'048} + \frac{b}{108'064} = \frac{x}{e} \quad \dots \quad (4).$$

$$\frac{108'064 - e}{e - 94'048} = \frac{108'064 a}{94'048 b} \quad \dots \quad (5).$$

Of the above quantities, n is known and is the amount of iodine disappearing or absorbed:—
 m is known and is the amount of the mixture of cresols and phenol weighed out into the solution.

x, y, e, a, b are five unknowns, and with the five independent equations given, they may be obtained.

This method is limited since the amount of the mixture m is obtained by weighing, and no impurity can be present without affecting the results. Further, it can be seen from the nature of the equations containing e that small variations in the determination of e affect the value of a and b considerably. However, if the dried precipitate of the iodo compounds were weighed after the titration with the thiosulphate a different value for m would be obtained; m would then represent the weight of the halogenated mixture, not the mixture itself. Equation (1) will become—

$$x + y + (127.96) N/2 - (1.008) N/2 = m.$$

The equation is useful for analysing mixtures containing water and other compounds which do not halogenate and which prevent the weighing of the mixture before precipitation with the iodine. The determination by the iodine and sodium bicarbonate is as accurate as the operator chooses to make it. Using large volumes of solutions (50 cc.) and allowing at least eight minutes for the solution to run out of the 50 cc. burettes, very accurate results can be obtained.

Table VI. gives the results of three successive titrations of a mixture composed of equal volumes of solutions of phenol, *o*-, *m*-, and *p*-cresol having the following strengths:—

Phenol	= 0.09060 N.
<i>o</i> -Cresol	= 0.06800 N.
<i>p</i> -Cresol	= 0.06800 N.
<i>m</i> -Cresol	= 0.09850 N.

The second last column gives the amount of iodine absorbed by the mixture. The last column gives the amount which should have been absorbed calculated from the amount of materials added to the mixture. The error varies from 2 parts to 5 parts per thousand. If the discrepancy be calculated over the four ingredients the error is 0.2 to 0.5 per cent. If the error be calculated as due to one single substance present the determinations vary by 0.8 to 2.0 per cent, since the substances are present in equal amounts by weight.

Determination of Thymol.

The assumption is very general in the literature that time is an important factor in the halogenation of aromatic compounds. This is especially true for the more highly substituted phenolic bodies. Fifteen minutes to one hour is recommended as the time for complete halogenation. The assumption that this rate of reaction is comparatively slow seemed untenable. If complete diffusion be effected by continuous shaking the reaction should be complete in a very short time. To test this, the determination of thymol (3-methyl-6-isopropyl phenol) was undertaken.

The iodine-sodium bicarbonate method was applied to the determination of thymol and the results are given in Table VII. The calculations are made for the thymol strength, assuming that two iodines enter the ring giving di-iodo-thymol.

Experiments 33 and 34 show that the iodination is complete in one minute. Seidell states that one half-hour must be allowed for thymol to be brominated. This is true only in case the diffusion is incomplete (*Am. Chem. Journ.*, 1912, xlvii., 519). If the free iodine is in excess (300 per cent), as in Experiment 35, the hydroxyl is partly filled with iodine and gives a determination 22 per cent too high, calculated as the di-iodo-thymol. Experiment 36 indicates that the iodine which is absorbed in the hydroxyl will be freed in a few minutes if the precipitate is left in contact with the small amount of hydriodic acid, which has been formed in the solution. The reduction can be seen in the rapid return of the blue colour. This return of the blue continues only until the iodine in the hydroxyl has been completely liberated. An addition of 5 cc. of 20 per cent KI reduced the di-iodo-thymol bromide in one minute to the di-iodo-thymol and the blue colour does not return rapidly (*i.e.*, within one hour).

In working with the cresols and phenol the blue did not return except in the case of the ortho-cresol. The reading was taken after the blue ceased to return (five to ten minutes). No KI was added. However, it is advisable to use KI if the experiments show a tendency for the blue colour to return within five or ten minutes. The free hydriodic acid produced in the acid solution by this addition reduces (Werner, *Jahresber.*, 1866, 633; Lloyd, *Journ. Am. Chem. Soc.*, 1905, xxvii., 16) the thymol iodide completely, with one minute's shaking. Wilkie states that his determinations were all high (1½ per cent). The explanation lies probably in the fact that the iodine is partly absorbed into the hydroxyl, and as the iodo precipitate is filtered off in his method there is no possibility of its reduction.

Directions for Determining Phenolic Compounds.

First. Solutions required:—0.1 N sodium thiosulphate, 24.8 grms. per litre; 0.03 N iodine solution, 12.7 grms. per litre; N sodium bicarbonate; 2 N sulphuric acid; 0.5 per cent starch solution.

Second. Into a 500 cc. ground stoppered bottle, put 50 cc. water and 50 cc. of approximate N sodium bicarbonate, add 15 cc. of the unknown solution of the phenolic compound which has been previously diluted to approximately 0.1 N.

Run in the iodine solution until the mixture in the bottle remains a permanent brown iodine colour; 20 per cent excess is recommended. Stopper the bottle firmly and shake it well for one minute.

Third. Add carefully, at first, to prevent excessive bubbling, 50 cc. of 2 N sulphuric acid. Shake well and titrate the excess iodine with the thiosulphate, using starch as indicator. Occasionally blue colour returns rapidly after the end-point has been first reached. For such determinations it is best to add 5 cc. of 20 per cent KI to hasten the freeing of the iodine which is held in the hydroxyl. The final end-point after the blue ceases to return is the correct reading for the thiosulphate. All the solutions should be at 20°–25° C.

Summary.

I. Rapid and accurate determinations of *o*-, *m*-, and *p*-cresol, phenol, and thymol have been effected by the use of iodine solutions in the presence of sodium bicarbonate.

II. The method is equally rapid and accurate for all five compounds, the error for each compound being within 0.2 per cent.

III. The "reaction period" for these determinations is one minute, when the shaking is continuous.

IV. The sum of the cresols present in a mixture may be determined within a total error of 0.2 per cent; the *m*-cresol may be determined in the presence of *o*- and *p*-cresol by this method.

V. A series of simple equations are given which will permit the determination of phenol, meta-cresol, and the sum of the ortho- and para-cresols in the presence of each other in any combination or proportion if two quantities be known.

a. The weight of the mixtures taken.

b. The amount of iodine absorbed.

VI. Results of experiments are given which show that these four compounds can be determined in the presence of each other by this method within an error of 0.2 to 0.62 per cent, calculated on the sum of the materials present.

Gases Retained by Silver.—Ph. A. Guye and F. E. E. Germann.—A specimen of extra pure commercial silver was fused in a quartz tube, and a current of pure dry hydrogen was bubbled through it, the metallic mass being allowed to cool and solidify in an atmosphere of hydrogen. On analysis it was found that all the oxygen in the metal had been expelled, but in 1 gm. there still remained 0.027 cc. of CO and 0.010 cc. of H₂O.—*Comptes Rendus*, clix., No. 3.

TESTS FOR DETERMINING QUALITY OF PAPER.

By K. B. LAMB.

A GOOD deal of interest in paper testing has been shown lately by those who use, buy, sell, or manufacture paper in quantities, and it is the purpose of this article to explain in a comprehensive manner just what tests are made in the paper testing laboratory and the commercial value of such tests.

Paper testing is, of course, primarily of value to the consumer, who is to be found in practically every line of business. Often large sums of money are spent on the item of paper alone, but as a rule the consumer has no way of judging the character or quality of the paper or its suitability to his particular needs, except through observation or the word of the salesman who is selling it to him, and who is, of course, chiefly concerned in making a sale.

That observation counts for a great deal in determining the suitability of a paper, and in the estimation of widely different types cannot be gainsaid, but can observation tell which of two writing papers is the better? They may look and feel much alike, and yet be widely different in quality and have many different properties. Mere observation cannot answer questions such as these:—How much rag stock is there present? How much wood-pulp? How much mechanical pulp, and how much chemical pulp? What is the weight per ream, what is the strength, and the strength in comparison to the weight? What is the folding endurance? What sizing materials are used, and how much? What is the proportion of loading materials present, &c.?

The answers to questions like the foregoing, while not meaning much to one who knows little about paper constitute the basis for determination of questions such as the following:—Will the paper in question stay white or turn yellow with age? Will it take ink well? Is it strong enough for the purpose to which it is to be put, and will it endure folding? Will it emboss well? How many sheets are there to the pound? Are you paying for paper or excess mineral loading? Will it expand little or much under diverse atmospheric conditions?

Another and probably the most important use to which accurate paper testing can be put is in relation to buying on specification. If he is wise the consumer will make the firms selling him the particular kind of paper he wishes submit samples and estimates. He will then have a chance to compare the kinds and qualities of paper on the market and the prices of the different firms. He gets a greater variety to choose from, and also, by letting it be known that the samples are submitted on specification, he gets the best price possible for the given quality of goods. Paper testing here performs the duty of determining which sample represents the best value for the money.

In controlling shipments paper testing is also of value as it shows whether the paper is up to specification and whether the consumer is getting what he contracted for. The United States Government a few years ago undertook to control all the paper used in the different departments by buying on specification and by testing shipments, and was in many cases actually able to get a better paper at a cheaper price.

In view of the foregoing it may be stated that paper testing in general is of use:—

(1) In determining the best value obtained from money paid; (2) in buying on specification, determining which paper submitted is most suitable and economical; (3) in insuring uniform deliveries and maintenance of quality.

The tests naturally divide themselves into three divisions with subdivisions as follows:—

1. Microscopical tests—

- (a) For character of fibre.
- (b) For proportion of each constituent.

- (c) For quality of fibre and pulp.
- (d) For character of process used to manufacture pulp.

2. Physical tests—

- (a) Bursting strength.
- (b) Tensile strength.
- (c) Thickness.
- (d) Folding endurance.
- (e) Weight per ream.
- (f) Absorption.
- (g) Expansion.

3. Chemical tests—

- (a) Percentage of ash.
- (b) Percentage of rosin size.
- (c) Percentage of animal size.
- (d) Qualitative tests for starch, acid, sulphur, chlorine, glue, loading materials, colouring matters, &c.

I. Microscopical Tests.

The microscopical examination is the most important of all, as it shows what stock has been used in making the paper. It shows the character of the fibres used, both through their physical appearance and the colours taken by them with various stains. The proportion of each constituent can be estimated within 5 per cent, and the quality of pulp and nature of beating is easily discernible to the practised eye. The character of the process used to manufacture the pulp can also be determined both by the appearance of the fibres, which in the case of mechanical pulp are much torn and mutilated, and by colour reactions with different stains, "Herzberg's stain," for instance, giving a blue colour with chemical wood-pulp, a yellow colour with mechanical wood-pulp, and a wine-red colour with rag stock.

Briefly the method of preparation for microscopical analysis is as follows:—Small representative samples of the paper are boiled with 0.5 per cent sodium hydroxide solution. This removes everything but the pulp which is broken up on shaking in a test-tube with a little water. Some of this pulp is next transferred to a microscope slide with a dissecting needle, the excess water removed, and a drop of the stain added. A cover glass is now placed on top of the fibres, and they are ready for examination.

II. Physical Tests.

The physical tests are also very important as they determine strength, weight, &c.

The bursting strength is found by clamping a sample of the paper in a machine over a rubber diaphragm which is expanded upward by glycerin forced from a reservoir by means of a screw feed, a gauge attached to the reservoir giving the pressure in pounds per square inch. By use of the rubber diaphragm a uniform pressure is obtained. The tensile strength is obtained by clamping a strip of paper in a machine which exerts a uniform and regular pull until the sample breaks, the breaking-point and also the elongation being carefully noted. Both tests give the strength of the paper, and are particularly useful in testing wrapping paper where strength is an important factor.

The determination of thickness is effected by means of a micrometer gauge. This gauge is provided with a spring which presses the plunger rod on the paper, thus providing a uniform pressure in every case. The thickness is read on a dial above in thousandths of an inch, it being possible to estimate to ten thousandths. This, combined with the bursting strength or tensile strength of the paper, gives the relative strength. Folding endurance is found by means of a machine in which a strip of the paper is clamped under a uniform tension and which folds the piece of paper back and forth until the latter breaks, the number of such folds being automatically recorded. This is a very useful test for papers which are subjected to much wear and tear. Weight per ream is obtained by weighing several representative sheets and calculating the total weight.

Absorption is mainly used to test the quality of blotting-papers, and is carried out by allowing strips of the paper of uniform width to dip into a beaker of coloured water, and finding how the water rises in a given time.

III. Chemical Tests.

Chemical tests are of use in showing the quality of the paper in those ways in which it is dependent upon the character, quality, and amount of materials used in its manufacture, aside from the pulp. They determine whether the paper is unduly loaded, whether it will turn yellow with age, &c., and are particularly useful in the case of coated papers, by affording means of determining the amount and quality of coating used.

The proportion of ash is found by incinerating a weighed quantity of paper in a platinum crucible. This gives the amount of mineral matter contained in the paper, which, in excess of certain limits for each class of papers, must be considered nothing but an adulterant. An examination of this ash gives the nature of the mineral loading. The proportion of rosin size present is found by a method based on its extraction from the paper by ether, and animal size (glue, gelatin, casein, &c.), by a modification of the well known Kjeldahl determination of nitrogen.

The character, quality, and amount of size used are important, as the lasting and waterproof qualities of the paper, as well as its ability to take ink well, are largely dependent on them. Tests for acid are important in papers which are used to wrap metal ware of any kind, as acids tends to tarnish anything with which they come in contact. Tests revealing sulphur or chlorine are of value as indicating that the pulp has not been completely freed from the liquors used in its manufacture, or in bleaching it; they are, of course, detrimental to the lasting qualities of the paper. Starch is a sizing material sometimes used.

—*Chemical Engineer*, xix., No. 1.

SOME NATURAL INDICATORS.

By H. W. BRUBAKER.

COHN, in his "Indicators and Test Papers," states that the colouring matter from roses (*Rosa Gallica*) gives a deep red with green fluorescence in alkalis and light red in acids. I found that the colouring matter from *Rosa rugosa* gives a green colour in alkalis, red in acids, and colourless between these two. The colouring matter was extracted by triturating the petals in a mortar with some sea sand and 95 per cent alcohol. This was then filtered and the filtrate evaporated to dryness somewhat above room temperature. Upon taking the red colouring matter up in water, most of the fatty substances were left undissolved. This water extract was of a very bright red colour. To preserve the solution, enough alcohol was added to make a 50 per cent alcoholic solution. The addition of the alcohol partly decolorised the solution. This solution, when used as an indicator, was changed to green by 0.1N NaOH and, upon titrating with 0.1N HCl, went through a blue-green to colourless and then to pink in the acid solution. The neutral point was coincident with the colourless point, which was changed to either green or pink by one drop of 0.1N NaOH or, 0.1N HCl, respectively. The fact that the neutral point is colourless is probably due to the mutual destruction of the coming pink by the going green or *vice versa*.

Upon titrating a 0.2 gr. sample of sodium bicarbonate with 0.1N hydrochloric acid, using methyl orange as the indicator, there were required 24.8 cc. of the acid. Upon repeating the titration, using the rose extract as indicator, the correct end-point was not recorded unless the solution was boiled to drive off the carbon dioxide, in which case exactly the same amount (24.8 cc.) of the acid was

Flower.	In NH ₄ OH.	In HCl.
Crimson geranium ..	Dark purple	Bright red
Orange-red geranium	Bright purple	Orange-red
Martha Washington geranium	Blue to greenish blue	Red
White geranium	Yellow	White
Mock orange (white)	Yellow	White
White pansy	Canary yellow	White
Purple pansy	Greenish blue	Red
Dark red pansy	Dark blue-green	
	(almost black)	Red
Yellow pansy	No effect	No effect
Yellow and brownish red colours, mixed pansy	The yellow unchanged	Unchanged
	The brownish red changed	Changed
Dandelion (yellow) ..	To dark olive-green	To blood red
Phlox	No effect	No effect
Begonia	Olive-green	Red
Nasturtium	Dark blue	Red
	Through olive-green to brown	Orange-red
Petunia	Greenish blue to green	Purple-red
Red rose	Greenish blue to green	Red
White rose	Yellow	White
Cut-leaf mallow	Blue	Red
Red poppy	Purple	Red
Field larkspur	Green	Red
Vetch	Green	Red
Bind weed { white ..	Yellow	White
	pink ..	Pink
	pink ..	Pink
	Lavender	Pink
	crimson ..	Crimson
Portulaca { blood red	Dark brown (almost black)	Blood red
	yellow ..	No effect
Bachelor button (purple)	Blue	Red
Clover { white	Yellow	White
	red	Green
		Red

required to give the colourless point. This indicator, therefore, behaves like phenolphthalein toward carbon dioxide. It is a weak acid substance. Rose test-paper, made by dipping filter-paper into the solution and drying, changed from green in alkalis to red in acids. It was found to be sensitive to one part of NaOH in 25,000 parts of water. The extracted colouring matter from several other species of roses behaved, in general, like the one described above.

The colouring matter from the Perennial Pea (*Lathyrus Latifolius*, L.) behaved in a manner similar to that from the rose, giving a green colour in alkalis, red in acids, and colourless at the neutral point. This substance, when extracted from the blossoms with 95 per cent alcohol, gave a nearly colourless solution, which acquired a slight pink colour on standing and which developed colour very sharply in either acids or alkalis.

The colouring matter from the Iris (Blue flag), extracted as described above with alcohol and evaporated to dryness, gave a purple substance which was taken up in water to separate it from fatty substances. This colouring matter changed to green in alkalis and red in acids, and, like the rose colour, gave a colourless solution at the neutral point. The alcoholic extract obtained from the purple Vetch gave the same colour changes. The principal colouring substance of each of the above flowers seems to be the same, or very closely related chemically, as it behaves, in general, the same in all cases toward acids and alkalis. It is probably the same substance as found in the hollyhocks and dahlias which is described by Cohn. If the original alcoholic extract of certain varieties of roses is evaporated on a water-bath, glucosides present decompose, giving rise to a large amount of caramel which obscures the natural red colouring matter. The petals of

most flowers, especially the blue, red, pink, purple, &c., ones change colour when placed in alkaline solutions and back to the original colour or to some shade of red when placed in acids.

The accompanying table gives a list of some changes noted.

It is noticeable that the yellows are not affected by acids or alkalis. The whites are changed to yellow by alkalis and back to white again in acids.

The reds and purples are changed to some shade of green or greenish blue by alkalis and usually back to the original colour or a brighter red colour by acids. These natural colouring substances seem to be quite generally acid in character, in some cases neutral.

When it is observed that a certain flower or species of flower presents several different colours or shades of colour, the question naturally arises, does each of these colours represent a different chemical compound?

Judging from the above observations, it seems likely that nature makes use of comparatively few basal colouring substances with which to produce many different colours by means of slight chemical changes. These substances are generally acid, sometimes neutral in character, and generally change colour in acids and alkalis, alternately, acting as indicators. It is noticeable also that many of them are very sensitive to the action of light and air. The faintly coloured alcoholic solutions of the rose or the perennial pea, when evaporated to dryness, leave the bright red coloured substance. The pink blossoms of the perennial pea, when picked and allowed to wilt, change to a violet colour. The whole subject of natural colouring matters deserves a careful study from the chemical standpoint.—*Journal of the American Chemical Society*, xxxvi., No. 9.

TESTS FOR GALVANISED PRODUCTS.*

THE outward appearance of any galvanised article is not necessarily an indication of its excellence. This statement may be taken as a general rule applying to articles coated by either of the galvanising processes mentioned herein.

For over forty years prior to 1880 the hot galvanising process, which was practically the only galvanising process in commercial use prior to that time, was believed to produce uniform results. It was, therefore, not deemed necessary to test such coatings by any other means than that of durability under actual weather conditions. Observations made by Sir W. H. Preece, chief of the British Post Office Telegraphs, led him to see the necessity of a test for zinc coatings on telegraph wires.

Between 1880 and 1890 Preece devised what is known as the "copper sulphate test" for galvanised articles, and this test has until recently been accepted as the final word regarding the quality of any galvanised product. This test has been modified and standardised in the United States, notably by the chief engineer of the Western Union Telegraph Company, and has been generally adopted by producers and consumers of galvanised products, such as wire, sheets, line material, &c.

The original Preece test consisted in the immersion of the galvanised article in a saturated solution of copper sulphate for a period of one minute, removing, rinsing in water, wiping, and again immersing in the copper sulphate solution. The number of immersions which the article could withstand before showing bright copper on the underlying steel or iron was taken as an indication of the excellence of the zinc coating.

As at present standardised, careful preparation of the copper sulphate solution is necessary. The solution is

brought to a density of 1.186 specific gravity at a temperature of 65° F. This solution is usually treated with a small portion of cupric oxide to neutralise any free acid which might exist in the copper sulphate crystals. Galvanised articles are first to be cleaned of dirt and grease by immersion in gasoline or benzine, then rinsed in water and wiped dry.

After this preparatory treatment the articles are given successive one-minute immersions in the standard copper sulphate liquor, held at a temperature of from 65° to 70° F., rinsed thoroughly in water, and wiped dry after each immersion. The samples are to be carefully scrutinised after each immersion, and if spots of a clear copper colour are observed, the coating is said to have failed. The number of successive immersions which the article will withstand without showing indications of clear copper colour is taken as an indication of the quality of the coating. A new portion of solution is to be taken for testing each article.

It will be noted that the Preece, or copper sulphate test, determines only the thickness of the zinc coating at its thinnest portion. It is, therefore, not in any sense a determination of how much or how little zinc is deposited on the article under test. It is well known that the copper sulphate test is unsuitable for testing Sherardised articles, and it is a fact, however not generally known, that the copper sulphate does not attack zinc coatings deposited electrically, and by hot galvanising methods at equal rates. It has been further demonstrated that the different temperatures of the molten bath and different methods of cooling articles galvanised in molten zinc show entirely unreliable results when subjected to the copper sulphate test. From these remarks it will be seen that it is unfair to test competitively zinc coatings applied by Sherardising, hot-galvanising, and electro-galvanising methods.

Owing to the unsatisfactory results secured by means of the copper sulphate test, in a measure pointed out in the preceding paragraphs, an accurate quantitative test for galvanised products has been devised. The lead acetate test, as it is known, was recently originated by Professor W. H. Walker, of the Massachusetts Institute of Technology, Boston.

The test is designed to show the weight of actual coating covering products galvanised by any of the well-known methods. It takes into consideration the impurities residing in the coating, and the main impurity usually found—i.e., iron—may be determined if desired. In practice, however, it is seldom carried out to this extent. The solution employed removes from the articles both the zinc and zinc-iron alloys present. The accurate weight before and after testing furnishes the basis for computing the quantitative value of the coating. It is unnecessary to take the time of sample immersion accurately, in which respect the lead acetate test differs from the copper sulphate test; however, the weighings, which must be accurate to 1 mgrm., require considerable time and care. The lead acetate solution is prepared as follows:—

Dissolve 3 lbs. of commercial lead acetate crystals, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$, in 1 gallon of distilled water, and add 1 oz. litharge (PbO). After complete solution of the lead acetate, the mixture should be stirred vigorously, and any undissolved residue allowed to settle. The clear liquor is then poured off, and the solution is ready for use. It is unnecessary to maintain any accurate temperature of solution, as is required in the copper sulphate test, and the solution may be used for several tests without renewal until such time as the action becomes too slow.

Samples of galvanised product are first to be thoroughly cleaned of oil and dirt by rinsing in benzine or in gasoline, then rinsing in cold water, and dried with clean cotton waste. The sample should next be weighed to an accuracy of 1 mgrm., and the weight noted. The sample is then ready for immersion in the lead acetate solution.

The length of time during which the sample is under treatment is usually about three minutes, although it may

* From a pamphlet, "The History and Development of the Galvanising Industry," issued by the Mesinger Co., Chicago, Ill.

be left in for a longer period without affecting the result. These immersions should be repeated until all of the coating has been removed and the sample exhibits the clean steel underneath. A short experience will enable the operator to tell with certainty when all of the coating has been removed. After each immersion in the lead acetate solution the flocculent, or loose coating of spongy lead which is deposited, must be carefully removed; for this purpose it is usual to employ a soft, small bristle brush, care being taken that no lead is "burnished" over the zinc coating. If any spots of lead are noted which the solution does not remove, the careful use of a sharp knife is necessary. When the coating is all removed, the sample is then dried by immersion in alcohol and ignition, or by placing over a small steam coil. Final weight of the sample is then taken and noted.

If it is desired to estimate the amount of iron in the coating, the samples must be rinsed in clean water contained in a beaker, care being taken that all lead acetate and solution washings are saved. The lead acetate and the wash solutions may be put together and filtered, and slightly acidified with sulphuric acid; a few particles of granulated zinc should then be added, when the amount of iron is ascertained by titrating the solution with a standard solution of potassium permanganate. The lead may be balled and squeezed with the fingers, and saved if desired.

The lead may be weighed and the amount of zinc coating removed may be calculated from the weight of the lead; the preferable manner of determining the amount of coating on the sample under test is as follows:—Deduct the final weight of sample after treatment in the lead acetate solution from the original weight of the galvanised piece. Divide the net weight of coating so obtained by the weight of the bare or uncoated sample, whence the percentage of loss in weight is ascertained nearly enough for all practical purposes. Apply the percentage loss figure to 2000 lbs., representing a ton of the articles in question. This will give the pounds of coating per ton of product.

Next, ascertain by close measurement or estimation, how many square feet of surface there are in a ton of 2000 lbs. of the articles under examination, reducing the pounds coating per ton, found by the application of the percentage figure, to ounces by multiplying by 16. Having the ounces of coating per ton and the number of square feet of surface per ton, divide the former figure by the latter, and find the ounces per square foot; this is usually a decimal figure. The ounces of coating per square foot gives a unit which may be used for the purpose of comparing the values of coating on different styles and kinds of galvanised product.

Samples of galvanised articles which are to be given the lead acetate test must be, above all things, smoothly galvanised, without adhering lumps or drops of spelter, since these imperfections would lead to erroneous conclusions by adding to the net weight of coating particles of metal not evenly distributed, wherefore the resultant ounces per square foot would be too high. It should be carefully observed that all portions of the galvanised article are coated unless the uncoated areas are left out of the area figure per ton.

Professor Walker has rendered further service to those interested in testing galvanised materials by supplying a test which will show the presence or absence of pores or cracks in zinc coatings.

A strong solution of caustic soda in water is heated to a temperature of about 210° F., and the galvanised article suspended in this solution by a string or other non-metallic suspension. If pin holes or cracks exist in the coating, bubbles of hydrogen will be observed to come from the surface of the article at these points, while if there are no pores or cracks in the coating no action will be observed. The caustic soda test will show whether or not the coating has cracked when the galvanised article is bent after galvanising.—*Chemical Engineer*, xx., No. 1.

A METHOD FOR THE RAPID QUANTITATIVE ANALYSIS OF BRONZE AND BRASS.*

(Pb, Cu, Sn, Sb, Fe, and Zn).

By RICHARD EDWIN LEE, JOHN P. TRICKEY, and
WALTER H. FEGELY.

Introduction.

THE method of analysis reported in this paper is the outgrowth of an investigation that was undertaken as the result of a request made to one of us some time ago to take charge of some "control" work for a large company manufacturing bronze metal in various forms. Most of the metal is sold on specification. The alloy supplied by this firm varies in composition as follows:—Cu, 65 to 69 per cent; Pb, 25 to 30 per cent; Sn, 5 to 6 per cent; Fe, 0.1 to 0.3 per cent; Zn, 1.5 to 3 per cent. The requirements were that the analysis be accurate to 0.2 per cent and that the time consumed in making the complete analysis should not exceed one hour, preferably forty-five minutes.

On receipt of this request the authors began immediately to make a careful survey of the literature relating to the analysis of bronze and brass in the hope that it would be possible to find a method adapted to their needs. Over two months were devoted to testing the various proposed methods with "known mixtures" of the metals comprising the alloy. The authors hesitate to say whether the fault lay with themselves or was inherent in the methods, but most discouraging results were obtained although each method was tested repeatedly with the exercise of much care. We were finally confronted with the following perplexing situation; on the one hand, such methods as were found to give the required accuracy were too long and tedious; on the other hand, the few methods proposed for rapid analyses failed in our hands to give not only the desired accuracy, but the accuracy claimed for the methods by their respective authors.

This experimental survey, however, was not without value, as it rendered possible not only the detection of inaccuracies in many of the recommended procedures, but the selection of the best processes involved in such of the proposed methods as most closely approximated our wants. Furthermore, it facilitated the formulation of conditions best adapted to securing the desired end.

Early in the investigation it became obvious that it would contribute greatly to the rapidity of the determinations if a method could be formulated which would provide for the using of a separate portion of the alloy for each determination. The more accurate of the proposed methods are as a rule, open to the serious objection that one portion of the alloy is used for several determinations. Such procedure, however, is time-consuming. In the method of analysis proposed in this paper all the metals are determined in separate portions of the alloy with the exception of zinc, which is determined in the filtrate from the iron if the latter is present. When the iron is absent from the sample the zinc is determined in a separate portion in about thirty minutes.

The authors make no particular claim to originality for the scheme of analysis submitted herewith as most of the methods are based upon reactions familiar to all chemists. Furthermore, some of them have been employed by Low, Demorest, P. H. Walker, and Whitman and other well-known contributors to industrial analysis as a basis of standard methods for single determinations. However, the modifications of the selected procedures and their application to the complete analysis of bronzes of the stated composition, the study of the sources of error, and the conditions most favourable for procuring the desired results by means of the adopted procedures together with the formulation of such new processes as were necessary

* Presented at the 49th meeting of the American Chemical Society, Cincinnati. From the *Journal of Industrial and Engineering Chemistry*, vi., No. 7.

to articulate the different procedures, are some of the problems which have been attacked.

The accuracy of the methods is shown by the experimental results recorded in Part II., Test Experiments. As a further confirmation of the dependability of the method it may be noted that the procedure described herein has been used with equally good results not only by the students in this laboratory but also by the chemists in one large testing laboratory (the Meadville Testing Laboratory, Meadville) for a period of nearly three months.

PART I.—METHOD OF ANALYSIS.

Determination of Lead.

Procedure.—To 0.5 gm. of the alloy in a 300 cc. Erlenmeyer flask, add 12 cc. of water containing 4 grms. of tartaric acid, and then 4 cc. of conc. HNO_3 . Place on a hot plate to dissolve the alloy quickly. (The solution should be perfectly clear; if not, reject it and repeat the procedure). Remove the solution from the hot plate, allow to cool for one to two minutes, add 10 cc. conc. H_2SO_4 , and then heat on hot plate until all nitrous fumes are expelled. (Caution: Care must be exercised not to carry the procedure beyond this stage or the tartaric acid will be decomposed). Dilute with 100 cc. of cold water, add 75 cc. of ethyl alcohol, shake, allow to stand for two or three minutes, filter through a weighed Gooch crucible, wash with water to which a little H_2SO_4 has been added, until the precipitate is white, and then wash out acid with alcohol. Reject the filtrate. Dry the precipitate in crucible on hot plate, and then heat to dull redness with the Bunsen burner for a few minutes. Cool and weigh as PbSO_4 .

$$\text{Wt. PbSO}_4 \times 0.683 = \text{wt. Pb.}$$

Notes.

1. In order to prevent occlusion and adsorption of the Cu salts by the lead sulphate precipitate, it was found necessary to make the solution from which the lead precipitate is separated by filtration relatively large. The solution of the lead sulphate is prevented by the addition of alcohol.

2. In case the alloy contains a small percentage of lead, it is advisable, of course, to use a relatively large amount of the sample. If this is done, the quantities of the reagents employed, including water and alcohol, should be increased proportionately. The reasons for this procedure are obvious. In the first place, unless the volume of the solution is made larger the concentration of the Cu and other metals present becomes very large owing to the use of larger amounts of sample. This will increase the error due to occlusion and adsorption as mentioned in Note 1. In the second place, in order to preserve the proper concentration of sulphate ions for the complete precipitation of Pb in this larger volume of solution it is necessary to use larger amounts of the reagent, sulphuric acid.

Determination of Copper.

Procedure.—Place 0.5 gm. of the alloy in a 400 cc. beaker, add 5 to 10 cc. of dilute HNO_3 (1—1), cover beaker with a watch-glass until violent action ceases, then remove watch-glass and evaporate on hot plate to syrupy consistency. Dilute to about 200 cc. and add KOH solution until a small precipitate of copper hydroxide persists after thorough stirring. Now add acetic acid until the copper precipitate is completely dissolved, then add a small excess of the acid. Cool the mixture to tap-water temperature, then add 40 cc. of the KI solution (100 grms. to 1 l.) and 5 cc. of starch solution, and titrate immediately with standard $\text{Na}_2\text{S}_2\text{O}_3$ solution until the blue colour disappears.

Notes.

1. It has been pointed out by Walker and Whitman (*Journ. Ind. Eng. Chem.*, 1909, i., 519) that the results obtained by following Low's iodide method (*Journ. Am. Chem. Soc.*, 1902, xxiv., 1082) are uniformly a little low.

They add "this error is not due to the method which gives exceedingly accurate results, but to the fact that nearly 6 per cent of the copper is not precipitated as cuprous oxide. This loss is uniform, for if we add 6 per cent of the copper determined, the result will be the per cent of the copper in the alloys." This is undoubtedly true. Their further statements, however, that when an alloy containing 5 per cent of copper is decomposed by nitric acid, evaporated to dryness, taken up with nitric acid and filtered, the error in determining the copper in the filtrate will frequently be 0.5 to 0.7 per cent, cannot be confirmed by our experience. By following the proposed method of standardisation and analysis, which is essentially Low's method, we have been able to check within 0.1 per cent repeatedly.

2. Provision has not been made in the method as formulated for the separation of copper from any other metals, yet care must be exercised to exclude from the solution prepared for titration any substances which will either liberate or absorb iodine. Therefore, free Cl, free Br, nitrous oxides, ferric ions, and As and Sb in the "ous" condition must be absent.

Ferric ions may be removed by adding ammonium fluoride, which interacts with the former to produce ferric fluoride. This latter substance which is only slightly ionised has little or no oxidising power, and, therefore, cannot liberate iodine under the existing conditions.

The trivalent arsenic and antimony, if present, must be oxidised to the pentavalent condition by the addition of bromine. Excess of bromine must be removed by boiling the solution before titrating.

No other elements interfere with the procedure.

3. Pb, Bi, and Cd, if present, interact with the KI and form the corresponding yellow insoluble iodides. This causes no trouble, however; in fact many chemists regard the presence of one or more of these metals as a distinct advantage as the presence of the yellow precipitate assists the operator in securing uniform end-points. In this laboratory it is customary to add a few cc. of a solution of lead acetate to the solution to be titrated if it is known that Pb is not present.

4. In order that the liberated iodine may be held in solution it is necessary to use rather large excess of KI. This procedure increases the speed of the reaction.

5. The presence of an excess of inorganic acid interferes with the procedure. It should be remembered, however, that unless the solution contains a sufficient excess of acetic acid the end-point will not be sharp.

6. The solution should always be cooled to tap-water temperature just before the KI solution is added.

7. It should be remembered that the Sn present will make an insoluble residue in the solution prepared for titration.

Determination of Tin (and Sb).

Procedure.—Weigh 0.5 gm. of the alloy into a 400 cc. beaker, add 5 to 10 cc. of dil. HNO_3 (1—1), cover with a watch-glass until violent action ceases, then remove cover and evaporate to a paste on hot plate. Add 15 cc. of dil. HNO_2 , boil for several minutes, and dilute to about 200 cc. Boil for a few minutes, filter through a weighed Gooch crucible, wash with hot nitric acid wash, and then with hot water. Pour the filtrate into a 500 cc. beaker and reserve for check determination of copper. Dry the crucible and contents on hot plate and then ignite at red heat for ten minutes. The ignited residue consists of SnO_2 and any Sb (as Sb_2O_3) which may have been present in the alloy.

$$\text{Wt. SnO}_2 \text{ (and Sb}_2\text{O}_3) \times 0.788 = \text{wt. Sn (and Sb).}$$

Notes.

1. The results obtained by this method are usually a little high, owing to the fact that the precipitate frequently contains traces of the oxides of Cu, Sb, and Pb. However, the digestion of the dried residue in dilute nitric acid and the final separation of the precipitate from a large volume of solution, tend to reduce errors from this source.

The precipitate will also contain any phosphorus that is present in the sample.

2. Much time and energy were consumed in an effort to obtain a volumetric method for determining tin in a separate portion of the alloy. One of the most attractive volumetric methods for making this determination is Walker and Whitman's modification of Low's iodometric method (*Journ. Ind. Eng. Chem.*, 1909, i., 519) 519). Our efforts, however, to adapt it to our scheme of analysis were without success. The chief obstacle to its application to the rapid analysis of bronze is the presence of relatively large percentage of Cu in the alloy. The method, however, was found to give excellent results when used in making analyses of Babbitt metal if the percentage of Cu in the alloy was small; but if the percentage of Cu was large the results came high, owing to the fact that during the reduction of the Sn the Cu was reduced to cuprous chloride which takes up a portion of the iodine when the solution is finally titrated. Our results in regard to the error introduced by the titration of Sn in the presence of Cu agree with those obtained by Ibbotson and Aitchison (*CHEM. NEWS*, 1913, cviii., 109; also *Chem. Abs.*, 1913, vii., 2025; 1914, viii., 476).

(Check Determination of Copper).

Procedure.—Cool the filtrate from the Sn determination, add KOH solution until a small precipitate of copper hydroxide persists after thorough stirring. Add acetic acid until the copper precipitate is completely dissolved, then add a small excess of the acid. Follow directions as given under Determination of Copper.

Determination of Antimony.

Procedure.—Weigh out 0.5 grm. of the fine drillings of the alloy into a 300 cc. Kjeldahl flask, add 25 cc. of conc. sulphuric acid and heat over the bare flame of a Bunsen burner. Keep the acid at its boiling-point until the solution is clear or the residue is white. Cool, add 100 cc. of water, boil for several minutes and transfer the contents of the flask to a 400 cc. beaker. Dilute to 200 cc., heat to 70° C. (158° F.) and titrate with a standard KMnO_4 solution. The permanganate solution should be added rapidly until the permanganate colour persists, then add several cc. in excess. Stir the solution vigorously, and then titrate with a standard solution of ferrous ammonium sulphate until the pink colour just disappears.

Notes.

1. Although antimony is not found in the majority of bronzes and brasses it frequently occurs alloyed with variable percentages of lead, tin, copper, and iron. Therefore, in order to make the present scheme of analysis as wide as possible in its application and thereby increase its usefulness, it was deemed advisable to incorporate a method for the rapid determination of Sb.

2. The method is at once recognised as a modification of Low's well-known method (*Journ. Ind. Eng. Chem.*, 1913, v., 842). The chief difficulty we experienced in fitting it to our scheme of analysis was the matter of securing Sb in a suitable condition in sulphuric acid solution. Alloys containing a high percentage of copper resist solution by the usual procedure. Nitric acid is eliminated as a solvent because of its oxidising action; and HCl and KClO_3 are ineffective unless the treatment is greatly prolonged. Finally, the not-entirely satisfactory method of decomposing the alloy in conc. sulphuric acid in a Kjeldahl flask exposed to the bare flame of a Bunsen burner was adopted. Complete decomposition is usually effected in ten to twenty minutes, after which the determination may be readily finished in ten minutes.

After one or two trials it will probably be found that the blue colour imparted to the solution by the presence of the copper does not hinder the determination of the exact end-point when the permanganate is added.

3. Demorest has pointed out in an excellent paper (*Journ. Ind. and Eng. Chemistry*, 1913, v., 842) that it

is necessary to employ a large excess of potassium permanganate to complete the oxidation of the Sb. It is not best to have HCl present when the antimony is titrated, as the end-point is made very transient by its presence.

(To be continued).

OBITUARY.

DR. E. RILEY.

WE regret to have to announce that the death of Dr. E. Riley has recently taken place at the age of eighty-three years.

Dr. Riley, who was chemist at the Dowlais Iron Works in South Wales from 1853 to 1859, had done valuable work in analytical chemistry and metallurgy, and, in particular, he took an active part in the working out of the Bessemer steel process. Thus it was due to his suggestion that the lining of the converters was made from a mixture of dolomite and dry tar, and he published many analyses of metallurgical products, such as blast-furnace dusts, slags, &c. He made a thorough investigation, in collaboration with Gilchrist, of the nature of Canadian iron ores and their distribution, and he also made an exhaustive study of the influence of the presence of chromium and vanadium on puddled iron.

NOTICES OF BOOKS.

A First Book of Chemistry. By W. A. WHITTON, M.Sc.
London: Macmillan and Co., Ltd. 1914.

THIS is a successful little "first book" on chemistry, and the author's aim of stimulating his readers' interest and thus inducing them to read further, is likely to be thoroughly fulfilled. Although it shows no striking originality the facts of elementary chemistry, and especially those which bear on everyday life, are clearly explained, and illustrative experiments are described. These can usually be performed by the student himself with simple apparatus, and full directions are given which should enable him to obtain successful results without very much help. The more important non-metallic and metallic elements are included, and at the end of the book a chapter is given to the consideration of the laws of chemical combination. The book contains some questions and easy miscellaneous exercises, many of which have been selected from recent papers set in the Oxford and Cambridge Local Examinations.

Roberts-Austen. A Record of His Work. Compiled and Edited by SYDNEY W. SMITH, B.Sc. (Lond.), A.R.S.M.
London: Charles Griffin and Co., Ltd. 1914.

THE late Sir William Roberts-Austen occupied a unique position among metallurgists and among scientific men, and it was highly desirable that judicious selections should be made from his scattered works and published in a readily accessible form, a task which the compiler of this book has skilfully performed. An account is given of his work at the Mint and the Royal School of Mines, and many of the valuable addresses which he delivered and which are of special interest to students are reproduced in full. Several of the longer and more important of his contributions to the *Transactions and Proceedings* of the Royal Society are given in slightly condensed form, and some of his Addresses as President of the Iron and Steel Institute and Friday Evening Lectures at the Royal Institution are included.

CORRESPONDENCE.

NATIONAL RELIEF FUND.

To the Editor of the Chemical News.

BUCKINGHAM PALACE,
October 5, 1914.

ON August 6th I appealed to the Nation to assist me in founding a National Fund to prevent and alleviate military and civil distress arising in consequence of the War. To-day, after the lapse of exactly two months, I am happy to say that the Fund has reached the splendid total of three million pounds. I wish to take this opportunity of thanking once more the many thousands of generous subscribers who have helped me to achieve this grand result.

I have delegated the responsibility of administering the Fund to the Executive Committee which I have appointed on the advice of the Prime Minister, and I count upon the Committee to see that assistance in emergency cases is adequate and given with as little delay as circumstances permit. I trust that the portion of the Fund which is to be applied in relief of civil distress may, as far as possible, flow into productive channels, such as assisting schemes for male and female employment and perhaps industrial training; for it is as repugnant to me as it must be to the recipients that assistance should be distributed only in the form of doles. What men most want is work, and what the young people need is training.

The sum which has already been raised is magnificent, and I am confident that the generous British public will continue to do their utmost to alleviate the distress which War inevitably brings in its train.

EDWARD.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clix., No. 3, July 20, 1914.

Catalytic Decomposition of Benzoic Acid.—Paul Sabatier and A. Mailhe.—Certain anhydrous oxides, which are good catalysts for alcohols and acids, are almost entirely inactive towards benzoic acid vapours, which pass over them unaltered. Such are zirconium and cerium oxides, and the blue oxides of tungsten and molybdenum. Reduced copper, cadmium, titanium, and zinc oxides decompose benzoic acid into benzene and carbon dioxide, while other catalysts produce more or less benzophenone, as well as benzene and carbon dioxide. Catalysts belonging to this class are lithium and calcium carbonates. With reduced nickel or nickel oxide, carbon dioxide, hydrogen, and methane are evolved, carbon being left. In the case of iron the benzene liberated is partially reduced to carbon, hydrogen, and hydrocarbons, and the benzene obtained always contains a certain proportion of diphenyl.

Optical Decomposition of Iridotrioxalates.—M. Delépine.—A solution of potassium irido-oxalate gives with dissolved strychnine sulphate the *d*- and *l*-irido-oxalates of strychnine, which are separable by fractional crystallisation, the salt of the dextro acid being the less soluble. The dextro potassium salt can be prepared by dissolving the strychnine salt in water, treating with the theoretical quantity of potash in the cold, separating off the strychnine, and evaporating the filtrate in the cold. Thus the synthetic iridotrioxalates, like the chromo- and rhodo-oxalates, can be split up into a *lævo* and a *dextro* salt.

Solid Chromic Sulphates.—A. Sénéchal.—The progressive dissociation of the sulphate $(\text{SO}_4)_3\text{Cr}_2 \cdot 14\text{H}_2\text{O}$ gives salts which can be classed in two groups. The first contains at least three definite species:— $(\text{SO}_4)_3\text{Cr}_2 \cdot 14\text{H}_2\text{O}$, $[\text{Cr}_2(\text{SO}_4)_3]_6$, $[\text{Cr}_2(\text{SO}_4)_3]_3$. These salts, recombine with water, and dissolve the more rapidly the more water they contain. Their molecular volumes obey the law of additivity. The second group contains the brown anhydrous sulphate and the products of the dehydration of $(\text{SO}_4)_3\text{Cr}_2 \cdot 3\text{H}_2\text{O}$. They are insoluble in water, and have in ordinary conditions only a very feeble chemical activity.

Bromine Hydrate.—H. Giran.—Thermic analysis shows that the hydrate of bromine is represented by the formula $\text{Br} + 8\text{H}_2\text{O}$, which theoretically contains 52 to 63 per cent of bromine. This result is confirmed by the analysis of the hydrate previously dried by centrifugation with kaolin, which completely absorbs the excess of water or bromine contained in the hydrate.

Oxalocitric Lactone and its Transformation into Tricarballic Acid.—H. Gault.—Under the influence of agents of hydrolysis and alcoholysis the ketolactonic chain of oxalocitric lactone either opens or does not, according as the reaction is performed at a high temperature (180° to 200°), or a medium temperature (100° to 120°). In the latter case hydrochloric acid transposes the lactone into coumaline-6-carbonic acid, water and alcohol not reacting. In the former case hydrochloric acid and water open the ketolactonic chain, giving on saponification a small yield of tricarballic acid. In the same conditions alcohol gives nearly the theoretical quantity of a mixture of tricarballic and propanetetracarballic ether which is transformed quantitatively into tricarballic acid by hydrochloric saponification.

MISCELLANEOUS.

Compounds of Monovalent Nickel.—L. Tschugaeff and W. Ichlopine.—When concentrated solutions of hydrosulphite and nitrite of soda are mixed in molecular proportions a reaction occurs, and the mixture acquires the property of giving with salts of nickel, NiX_2 , a blue or violet coloration. This coloration is due to the presence of two crystalline comparatively stable substances, one of which is violet and is much more soluble than the blue compound. For the former the authors suggest provisionally the formula $\text{H}-\text{N} \begin{smallmatrix} \text{SO}_3\text{Ni} \\ \text{SO}_3\text{H} \end{smallmatrix} \cdot n\text{H}_2\text{O}$. The addition of NaOH to a solution of this violet substance gives the hydrate $\text{Ni}(\text{OH})$, corresponding to monovalent nickel. This hydrate gives Ni_2S with sodium sulphide.—*Comptes Rendus*, clix., No. 1.

Literary Announcements.—Messrs. J. and A. Churchill announce for autumn publication the following new books:—"The Anatomy of the Human Skeleton," by J. Ernest Frazer, F.R.C.S.; with 219 illustrations, many in colours; now ready. "Medical Diagnosis," by Arthur Latham, M.D., F.R.C.P., and J. A. Torrens, M.B., B.S., M.R.C.P.; with about 100 illustrations, some in colours. "The Chemistry of Cyanogen Compounds, and their Manufacture and Estimation," by Herbert E. Williams. "Bricks and Artificial Stones of Non-Plastic Materials, their Manufacture and Uses," by Alfred B. Searle.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Nitronaphthalene, &c.—A correspondent would be glad to know the names of the makers of the following articles:—Nitronaphthalene, sulphocate of soda, sulphocate of ammonia.

THE CHEMICAL NEWS

VOL. CX., No. 2864.

THE FREEZING-POINT OF BENZENE AS A FIXED POINT IN THERMOMETRY.

By THEODORE W. RICHARDS and JOHN W. SHIPLEY.

THE transition temperatures of hydrated crystalline salts probably afford the most convenient and exact means of fixing points on the thermometric scale between 0° and 100° C. A number of these have been determined in the W. Gibbs Memorial Laboratory of Harvard University, chief among which are the transition temperature for sodium sulphate (Richards, *Am. Journ. Sci.*, 1898; Richards and Wells, *Proc. Am. Acad.*, 1902, xxxviii., 431), the dekahydrate of sodium chromate into hexahydrate and into tetrahydrate (Richards and Kelley, *Proc. Am. Acad.*, 1911, xlvii., 171; *Journ. Am. Chem. Soc.*, 1911, xxxiii., 847), the dihydrate of sodium bromide into the anhydrous salt (Richards and Wells, *Proc. Am. Acad.*, 1906, xli., 435), the transition of manganese chloride from the tetrahydrate into the dihydrate (Richards and Wrede, *Proc. Am. Acad.*, 1907, lxiii., 343, Univ. of Berlin), and the transition of dekahydrated sodium carbonate into the heptahydrate (Richards and Fiske, *Journ. Am. Chem. Soc.*, 1914, xxxvi., 486). These points are perfectly definite, subject to no appreciable change by ordinary changes in atmospheric pressure, and usually involve considerable latent heat of transition. Most of them are easily reproducible. For these reasons they are very useful in calibrating thermometers.

The use of the freezing-points of liquids for determining fixed points on the thermometric scale probably comes next to transition temperatures in regard to convenience. Freezing-points, like transition temperatures, are more constant than boiling-points, because the influence of change in atmospheric pressure is usually negligible. On the other hand, however, the purity of the substance chosen becomes a very important issue (Landolt, "Über die genaue Bestimmung des Schmelzpunktes Organischer Substanzen," *Zeit. Phys. Chem.*, 1889, iv., 349). Most liquids (except water and mercury) are very difficult to prepare in a pure state, and volatile impurities which scarcely affect the boiling-point may very seriously change the freezing-point. For this reason the transition temperature of pure salts are often preferable; such a substance as sodium sulphate is very easily purified by crystallisation.

In other respects the errors to which the two types of equilibrium are subject are very similar. Both are liable to super-cooling or super-heating in the hands of the incautious experimenter; but in both, these sources of error are easily and completely eliminated by the use of plenty of each phase concerned, by proper protection of the system from gain or loss of heat with the help of an air-jacket and a like surrounding temperature, and by adequate but not too violent stirring. In both, the point is sharper and more accurate the greater the latent heat of melting. This is not only because outside heating or cooling is more quickly taken up, when this is large, but also because the influence of foreign substances on the freezing-point is inversely proportional to the latent heat of fusion, provided that the crystals are uncontaminated by solute. This is expressed by a transposition of the well known equation of van't Hoff, $\Delta T = RT^2/Mw$, which gives the depression produced by 1 grm. of dissolved substance of molecular weight M dissolved in w grms. of solvent having a latent heat of fusion l per grm. The following table therefore shows that, whereas benzene is a good substance

for this purpose, such substances as cyclohexane and cyclohexanol (especially the latter) are very unstable.

Latent Heat of Fusion of Four Substances.

	Cal. per grm.
Water.. .. .	79.8
Benzene	30.1
Cyclohexane	8.8
Cyclohexanol	2.94

The presence of 0.001 per cent of water lowers the freezing-point of cyclohexanol by 0.02° (Richards and Shipley, in a research as yet unpublished), whereas the same amount of this impurity affects the freezing-point of benzene by less than 0.002° (Hertz, *Ber.*, 1898, xxxi., 2669).

Another property adds to the satisfactory nature of benzene for this purpose, namely, the possibility of freeing it from most of its impurities by fractional crystallisation or freezing. Thiophene, it is true, cannot be separated in this way, but this impurity may easily be removed chemically. On the other hand, paraffin hydrocarbons, olefines, acetone, and most other impurities are quickly eliminated from the successive crops of crystals.

The fact that the melting-point of these crystals is 5.5° above that of water—just the length of the usual Beckmann scale—makes it an especially useful fixed point, for, with the help of these two melting-points, any such thermometer may be easily standardised, and then, with the help of the well known correction factor, used with confidence at any other temperature—provided that due precautions be taken for correcting the result for the temperature of the exposed thread.

For these reasons it seemed to us worth while to make a careful study of this point, especially because the published work of others is conflicting with regard to it. Paterno gives three values, 5.53°, 5.55°, and 5.48° (*Gazz. Chim. Ital.*, 1897, xxvii., [1.], 481); while Lachowicz gives 5.42° (*Ber.*, 1888, xxi., 2206); and Young, 5.58° (*Proc. Roy. Soc. Dublin*, 1910, xii., 31, 385; *Trans. Chem. Soc.*, 1899, xl., 486). (Prof. Young, in private correspondence, has stated that not much pains had been spent upon thermometric precautions in his work. We are much obliged to him for the trouble he has taken in consulting his original records). The discord among these and other values is probably due to inaccurate thermometry.

As many of the observers were principally concerned with the purity of their benzene rather than with its absolute freezing-point, the constancy of the melting temperature and not its exact value was all that was needed, but of course for other purposes the exact point must be known.

Dr. F. Barry, in 1910, and Dr. H. S. Davis, in 1913, under the direction of one of us, prepared benzene in a very pure state in order to determine its heat of combustion as a standard of comparison for other organic substances. Their final values, as determined by our best thermometers, were 5.484° and 5.486° respectively. These results were entirely independent, as the necessary corrections had not been applied to the earlier thermometric readings when the later ones were made. Both experimenters determined the ice-point on standard thermometers immediately after taking the melting-point of the benzene. Neither of these investigations have as yet been published, but they will soon appear in print.

From this earlier work it was apparent that the true freezing-point of benzene probably lies between 5.48° and 5.50° with indication of the value 5.485°; yet more exhaustive work was needful in order to permit its use as a fixed point in thermometry. For this purpose we deemed it advisable to obtain benzene from two entirely different sources. Commercial "chemically pure" benzene procured from the distillation of a Pennsylvania coal-tar was the starting-point for one preparation, and another specimen consisted of benzene prepared synthetically from benzoic acid by a well-known German firm. The two

samples were carried through the same process of purification as follows:—

(a) About 600 cc. of the benzene were shaken with clean mercury. No darkening of the surface of the mercury was observed.

(b) The benzene was next shaken on a shaking machine (about 2½ hours each time) with six successive quantities of concentrated sulphuric acid. The acid was deeply blackened by the first four treatments, indicating the presence of substances charred by the action of strong acid, but the last two showed only a slight yellow coloration.

(c) The benzene was next washed with two quantities of water, and then shaken out with a concentrated solution of sodium hydroxide, followed by two more washings with water.

(d) Following this came another shaking out with mercury for about four hours. A considerable blackening of the surface of the metal was observed.

(e) After washing several times with water, the benzene was dried over calcium chloride and sodium, and distilled. Almost all of the product came over within 0.05°; that fraction distilling between 80.15° and 80.18° (uncorrected) was preserved for further purification.

(f) The benzene was next re-crystallised in porcelain, the coal-tar product six times, the synthetic five, and the fractions were preserved over sodium in glass bottles kept in the dark. The sodium was freshly cut, and allowed to stand for some time in the mother-liquor of the second crystallisation before being put through the sodium press.

Before determining the freezing-point of the purified samples of benzene, the excellent Beckmann thermometer to be used was carefully compared with a standard instrument, Baudin No. 15200, which had been standardised by the Bureau International des Poids et Mesures in Paris, and frequently used for the most accurate thermometric work in the W. Gibbs Memorial Laboratory of Harvard University (see *Proc. Am. Acad.*, 1902, xxxviii., 434; *Zeit. Phys. Chem.*, 1903, 443, 467). The Beckmann thermometer (P.T.R. 31827) was graduated in hundredths and covered a scale of six degrees, the length of a degree being 3.8 cm. It had been calibrated by the Physikalisch-Technische Reichsanstalt, Berlin, in 1907. The comparison of the instruments was carried out in collaboration with Dr. T. Thorvaldson, to whom we wish to express our gratitude for his kind assistance. The thermometers were compared at two points: the ice-point of benzene and the ice-point of water. The benzene used was commercial chemically pure benzene distilled and dried over sodium. Since the determinations were for comparative purposes only, the purity of the benzene was not yet in question, but the ice-point of water was, of course, carefully determined immediately afterwards under precisely parallel conditions.

The readings were taken immediately after vigorous stirring of the mixture and the two thermometers were read practically simultaneously. The measurement of the temperatures was carried out in accordance with the precautions pointed out by one of us in a recent publication (Richards, "The Measurement of Temperature in the Operations of Analytical Chemistry," *Orig. Comm. 8th Congress of Applied Chem.*, 1912).

In this way it was found that a range of 5.125° on the Beckmann corresponds to 5.104° as read on the corrected standard Baudin; or 1.000° as read on the former over this range of temperature corresponds to 0.9958° on the hydrogen scale. This was essentially the value given by the Reichsanstalt for this thermometer under these conditions.

The Beckmann apparatus was used in the freezing-point determinations, about 30 grms. of substance being employed. The apparatus was swept with a current of air dried with sulphuric acid and the benzene was distilled directly into the apparatus through the side tube, the thermometer and stirrer being already in place. The first third of the distillate was rejected. During the distillation, as well as during the determination, a slow current of dry air was allowed to pass in through the side tube,

thus preventing the access of moisture from the atmosphere. Such contamination was especially liable to happen during the operation of stirring. The benzene ice was present in varying quantities and conditions. The most satisfactory mixture was obtained by sub-cooling the liquid several degrees, and then, by vigorous agitation, producing a large crop of finely divided crystals. It was found, however, that so long as plenty of crystals were present the outside bath was not too cold, and adequate stirring was employed, the same constant freezing-point was obtained with both finely divided and large crystals. The purity of the benzene was indicated by the constancy of the freezing-point with diminishing proportion of mother-liquor, as the freezing progressed. Great constancy was observed in the fifth and sixth crystallisations of the coal-tar product, and in the fourth and fifth of the synthetic benzene.

Immediately after determining the freezing-point of benzene, the ice-point of water was taken in the same apparatus. Freshly distilled water was boiled and frozen under a variety of conditions; constant results were obtained with the same precautions as in the case of benzene; and this outcome was confirmed by the immersion of the instrument in a large bath of pure ice and water.

The ice points of water and benzene were thus observed in the same apparatus in the same way and with the same depth of immersion of the bulb and the same length of mercury column exposed to room temperature. The only stem correction necessary was that for the difference between the room temperature and the temperature of the freezing-point of benzene, applied to the number of degrees between the ice-point of water and of benzene.

The samples used in each trial were as follows:—

- A. Coal-tar benzene, fifth re-crystallisation.
- B. Coal-tar benzene, sixth re-crystallisation.
- C. Synthetic benzene, fourth re-crystallisation.
- D. Synthetic benzene, fifth re-crystallisation.
- E. Coal-tar benzene, fifth re-crystallisation.

Table I. summarises the results with the Beckmann thermometer P. T. R. No. 31827.

TABLE I.

Sample.	Constant Beckmann reading.	Ice-point.	Difference.	Total correction (a).	True temp.
A ..	5.822	0.300°	5.522	-0.038	5.484°
B ..	5.821	0.300°	5.521	-0.038	5.483°
C ..	5.772	0.249°	5.523	-0.038	5.485°
D ..	5.772	0.249°	5.523	-0.038	5.485°
E ..	5.760	0.237°	5.523	-0.038	5.485°

Average = 5.484°

(a) This correction was in each case -0.023 for the fundamental interval (1.000° on the thermometer = 0.9958 true degree) and -0.015 for the 5.50 stem exposed to the constant room temperature 23° or -0.038 in all.

Trials A and B were made on the same day; C and D were made about four weeks afterward; and E was made yet three weeks later. These tests show: first, that the coal-tar material (A, B, and E) was essentially identical (at least as regards melting-point) with the synthetic material; and secondly, that further re-crystallisation caused no change in the value. Hence the presumption is that these results give the true value corresponding to the pure substance.

Although these results are very concordant and indicate that the freezing temperature of benzene affords an accurate point for thermometric work, it was deemed advisable to take a series of observations directly on a Baudin standard instrument, in order to verify the absolute value of the above series of results. A shorter wide test-tube was substituted for the inside tube of the

Beckmann apparatus, and through the cork of this test-tube passed the Baudin thermometer, No. 15,200, and a narrower tube for the stirrer. This latter had a side arm, through which a current of dry air passed during the determination. The tube was submerged in the cool outside bath to within 0.5 cm. of the bottom of the cork, and the reading of the Baudin was made through the glass almost at the surface of this bath. By this means the necessity for any stem correction was obviated. The ice-point of water was taken immediately afterwards in the same apparatus with the same precautions. Four determinations were made on three successive days, the last two being made on the same day. The readings were verified in each case by Dr. Thorvaldson. In Table II., each observed reading listed is the average of a number of independent observations not varying between the extremes by more than 0.003°. The barometer readings for three days varied by only 3 mm., the readings being 763 mm., 762 mm., and 765 mm. respectively. Since the bulb of the thermometer was immersed to the same depth in each determination, the effect of the exterior pressure was identical in all four cases. The conditions of the experiments were so chosen that all other corrections were necessarily invariable.

TABLE II.
Corrections to be Applied.

	At ice-point benzene.	At ice-point water.
Calibration	+0.023	+0.002
Interior pressure ..	+0.015	+0.009
Exterior pressure ..	-0.001	-0.001
Fundamental interval ..	+0.004	+0.000
Stem	±0.000	±0.000
Total correction ..	+0.041°	+0.010

Final Readings, Observed and Corrected.

Determination.	Benzene.		Water.	
	Observed melting-point.	Corr.	Observed ice-point.	Corr.
F.	+5.688°	+0.041°	5.729°	0.208°
G.	5.686°	+0.041°	5.727°	0.207°
H.	5.688°	+0.041°	5.729°	0.207°
I.	5.689°	+0.041°	5.730°	0.207°

Determination.	Benzene m.p. corr. reading.	Water ice-point corr. reading.	F.p. benzene.	Hyd. scale corr.	F.p. benzene hyd. scale.
F.	5.729°	0.218°	5.511°	-0.030	5.481°
G.	5.727°	0.217°	5.510°	-0.030	5.480°
H.	5.729°	0.217°	5.513°	-0.030	5.482°
I.	5.730°	0.217°	5.513°	-0.030	5.483°

Averages 5.482°

This compares very satisfactorily with the values previously found, as follows:—

	Average values.	Variation from mean.	Max. variation between extremes.
Beckmann	5.484°	0.001	0.002
Baudin	5.482°	0.002	0.003

The true freezing-point of benzene may then be safely taken as 5.483°. This is only 0.001° different from the result of Barry, and 0.003° different from the latest and best trials of Davis.

The wide deviations of others are probably to be referred chiefly to doubtful thermometry, for benzene is evidently not very difficult to obtain in a pure state.

These experiments show that the freezing-point of pure benzene, 5.483°, is attained so easily that it may be used

as a very satisfactory fixed point in thermometry; and taken in connection with the freezing-point of water, about 5.5° below, may afford an excellent means of fixing two points on a Beckmann thermometer.

The authors are glad to express indebtedness to the Carnegie Institution of Washington for generous support in this investigation.

Summary.

The results of this research may be summed up as follows:—

1. Benzene pure enough for the purpose in hand is not difficult to prepare.

2. With due precautions in the thermometric measurements a very definite freezing-point is given by benzene. The true value is determined by constancy after repeated fractional crystallisation.

3. The freezing-point of benzene is 5.483°±0.002° on the international hydrogen scale.

4. This fixed temperature may be advantageously used, in connection with the ice-point of water, for calibrating Beckmann thermometers. Especial attention must be paid to the temperature of the exposed column in correcting this interval for use at other temperatures.—*Journal of the American Chemical Society*, xxxvi., No. 9.

A METHOD FOR THE RAPID QUANTITATIVE ANALYSIS OF BRONZE AND BRASS.*

(Pb, Cu, Sn, Sb, Fe, and Zn).

By RICHARD EDWIN LEE, JOHN P. TRICKEY, and WALTER H. FEGELY.

(Concluded from p. 185).

Determination of Iron and Zinc.

Procedure.—To 0.5 gm. of the alloy in a 400 cc. beaker add sufficient dilute HNO₃ (1:1) to dissolve the sample. Heat on hot plate until the alloy is thoroughly decomposed, then evaporate the solution just to dryness. Add 10 cc. of conc. HCl and 100 cc. of water, heat to about 70° C. and pass H₂S through the mixture until all the Pb, Cu, Sn, and Sb (Cd, &c.) are precipitated. Filter, using a Buchner funnel with an asbestos mat; wash the precipitate with water. The filtrate which contains the iron and zinc should be transferred to a 500 cc. beaker.

Note.

A drop of this filtrate should be transferred to a spot plate and tested with a drop of potassium ferrocyanide for the presence of Cu and Fe, which are interfering substances, and if present in weighable quantities they should be removed. If Cu is present, which will be indicated by the presence of red coloration, treat the filtrate again with hydrogen sulphide and filter; if Fe is present, which will be indicated by the appearance of a blue coloration, proceed as directed under (2), Iron and Zinc.

1. **Zinc, if Fe is Absent.**—Dilute the filtrate to 200 cc., heat to 70° C., and titrate with standard potassium ferrocyanide, using ferric chloride or uranyl nitrate as an indicator. The titration should be performed slowly and with constant stirring, in order to obtain the most satisfactory results. Continue to add the ferrocyanide until a drop of the solution in the beaker shows a bluish green tinge (brown tinge when uranyl nitrate is used as an indicator) when tested on a white porcelain plate with a drop of ferric chloride after standing a few seconds. The quantity of the standard solution which is required to produce a good end point in the blank determination made at the time of standardising the solution must be subtracted

* Presented at the 49th meeting of the American Chemical Society, Cincinnati. From the *Journal of Industrial and Engineering Chemistry*, vi., No. 7.

from the amount of standard used in making the determination.

Notes.

1. *Correction for Blank.*—As the indicators are not very sensitive under the imposed conditions, it is necessary to determine the excess of standard solution required to effect the colour change of the indicator used. A "blank" must be run, therefore, using the same quantities of reagents under corresponding conditions of volume, temperature, and acidity.

2. If the solution turns blue during the titration, it is an indication of the presence of small quantities of iron.

2. *Iron and Zinc.*—Add 2 cc. of concentrated HNO_3 to the filtrate to oxidise the Fe, heat to boiling, add 25 cc. of 5/N NH_4Cl , and then NH_4OH until the odour of the reagent barely persists after boiling the mixture for 1 minute. Filter off the $\text{Fe}(\text{OH})_3$ and ignite. Weigh as Fe_2O_3 .

Notes.

1. Zinc is completely precipitated from HCl solutions by potassium ferrocyanide as white zinc ferrocyanide. Such metals as Pb, Cu, Sn, Fe, and Mn are also precipitated by this reagent, and therefore must be removed before the Zn is titrated.

2. The acid solution must not contain free Cl, free Br, or the oxides of chlorine as these substances decompose ferrocyanide.

3. Care must be taken to conduct the standardisation as well as all determinations under corresponding conditions with particular reference to volume, temperature, acidity, amount of ammonium salts, and the rate of titration. Furthermore, it is imperative that the titration be conducted slowly and with constant stirring of the solution. If this precaution is not observed the end-point will be reached apparently before all the zinc is precipitated.

PART II.—TEST EXPERIMENTS.

In order to make a final test of the accuracy and general applicability of the procedures recommended in this paper, five series of experiments—each series consisting of six separate determinations—were made. In making this test, the results of which are reported herewith, a standard bronze alloy was used unless there is a note to the contrary. Equally good results were obtained when known mixtures were employed.

Series I.—Lead.

Number of experiment.	Wt. of sample. Grms.	Wt. of Pb present. Grm.	Wt. of Pb found. Grm.	Error percentage composition. Per cent.
1.	1.0055	0.0467	0.0469	00.02
2.	1.0005	0.0464	0.0465	00.01
3.	0.9995	0.0463	0.0464	00.01
1.	0.2013	0.1562	0.1559	00.10
2.	0.2114	0.1639	0.1642	00.15
3.	0.2266	0.1757	0.1754	00.15

A standard Babbitt metal was employed in making the last three determinations reported in the foregoing series.

Series II.—Copper.

Number of experiment.	Wt. of sample. Grm.	Wt. of Cu present. Grm.	Wt. of Cu found. Grm.	Error percentage composition. Per cent.
1.	0.5018	0.3042	0.3047	00.10
2.	0.5133	0.3112	0.3116	00.08
3.	0.5212	0.3160	0.3160	00.10
4.	0.4956	0.3009	0.3001	00.18
5.	0.5120	0.3104	0.3107	00.06
6.	0.5094	0.3088	0.3084	00.08

Series III.—Tin.

Number of experiment.	Wt. of sample. Grms.	Wt. of Sn present. Grm.	Wt. of Sn found. Grm.	Error percentage composition. Per cent.
1.	1.0000	0.0238	0.0242	00.04
2.	1.0000	0.0238	0.0251	00.13
3.	1.0000	0.0238	0.0252	00.14
1.	0.5000	0.0119	0.0120	00.02
2.	0.5000	0.0119	0.0123	00.08
3.	0.5000	0.0119	0.0122	00.06

Series IV.—Antimony.

A standard Babbitt metal, containing 77.53 per cent of Pb, 0.58 per cent of Cu, 10.03 per cent of Sn, and 11.65 per cent of Sb, was employed in making the tests, the results of which are recorded in the following series. In the first two determinations the Pb was removed as PbSO_4 before titrating with KMnO_4 ; in the following four determinations the titration was conducted in the presence of the PbSO_4 ; and in the last two determinations the titration was made in the presence of both Pb and Cu salts.

Number of experiment.	Wt. of sample. Grm.	Wt. of Sb present. Grm.	Wt. of Sb found. Grm.	Error percentage composition. Per cent.
1.	0.3000	0.0350	0.0349	00.03
2.	0.3000	0.0350	0.0349	00.03
1.	0.3000	0.0350	0.0349	00.03
2.	0.3000	0.0350	0.0359	00.03
3.	0.3027	0.0353	0.0354	00.03
4.	0.3027	0.0353	0.0356	00.09
1.	0.0327	0.0353	0.0354	00.03
2.	0.0327	0.0353	0.0354	00.03

The above results indicate that the presence of the Pb and Cu salts do not interfere with the titration of Sb with KMnO_4 .

Series V.—Zinc.

Number of experiment.	Wt. of sample. Grm.	Wt. of Zn present. Grm.	Wt. of Zn found. Grm.	Error percentage composition. Per cent.
1.	0.4985	0.1497	0.1492	00.10
2.	0.4969	0.1492	0.1497	00.11
3.	0.4975	0.1494	0.1497	00.06
4.	0.4977	0.1494	0.1495	00.02
5.	0.4979	0.1495	0.1496	00.02
6.	0.5004	0.1503	0.1505	00.04

PART III.—Summary.

I. A survey of a large number of proposed methods for the analysis of bronze and brass has been made. The majority of the methods have been found to be too long and elaborate; or if in the class of rapid methods, too inaccurate to be suitable even for control work.

II. A method has been proposed for the analysis of bronze and brass containing Pb, Cu, Sn, Sb, Fe, and Zn by which the determinations may be made with greater rapidity than any other methods of analysis known to the authors. Working with the usual laboratory facilities it has been found that after the samples have been weighed the determinations of Pb, Sn, and Sb in three different alloys can be easily completed in one and one-half to two hours.

III. The determinations made by this method not only agreed among themselves but they were more accurate than those made by the longer methods. The maximum error of any determination in any series was 0.15 per cent. The average error, however, is much less.

IV. The accuracy and general applicability of the proposed method has been shown by the series of test experiments, and further confirmed by the report of one commercial laboratory where the method has been constantly employed for nearly three months.

OZONE IN VENTILATION.*

By J. C. OLSEN and WM. H. ULRICH.

In spite of the fact that a great many investigations have been carried out in recent years on the effect of ozone on air bacteria and odours, and also on the physiological effects of ozone, the most diverse conclusions have been reached and opinions expressed with reference to the questions investigated. This confusion is due somewhat to faulty scientific technique and deductions from improperly chosen experiments as well as *ex parte* point of view. The most recent criticisms against ozone in ventilation are found in two articles which were published in the issue of September 27, 1913, of the *Journal of the American Medical Association*, one by Jordan and Carlson and the other by Sawyer, Beckwith, and Skolfield, on the bactericidal, physiologic, and deodorising action of ozone. A number of errors in the methods used in the experiments given in these articles have been noted, and these seem so serious and the articles have been so widely quoted that it seems desirable to correct the misapprehensions which have been produced. Both of these articles refer to the fact that exaggerated claims were made by agents selling ozone machines.

In the article by Jordan and Carlson, it is stated, on page 16, that the concentration of ozone is determined by drawing the ozonised air through a solution of potassium iodide which has been acidified with sulphuric acid. The liberated iodine is then titrated with thiosulphate solution. It is well known among chemists that an acidified solution of potassium iodide is readily oxidised by the ordinary oxygen of the air, and, therefore, if an acidified solution of potassium iodide is used for the determination of ozone, the results will be high. The amount of the error will vary with the concentration of the ozone, and may easily give results double the true concentration of ozone. This error can easily be demonstrated by drawing air free from ozone through such an acidified solution of potassium iodide. It is evident, therefore, that no reliance can be placed on the figures given for the concentrations of ozone which are reported in this article. In the article by Sawyer, Beckwith, and Skolfield, the concentrations of ozone were not determined.

It is universally recognised by ventilating engineers who are familiar with the use of ozone that it is of the greatest importance to regulate the concentration of the ozone, and that ozone is useful only when employed in the proper concentration. This well-known principle seems to have been so little understood by these investigators that they failed to make careful and accurate determinations of the concentrations of ozone used, and therefore many of the conclusions which they reached are entirely vitiated.

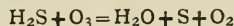
Another very serious error in experimental procedure is found in the tests which were made on the effect of ozone on odorous substances. A considerable number of such substances were experimented with, and the conclusion was reached that the ozone *masks* these odours but does not destroy them, and that, therefore, ozone is not useful in the removal of such odours.

The method of procedure consisted in exposing the substance giving off the odour until a marked odour was noticed in the small closed room which was used for the experiments. The ozone machine was then operated until a strong odour of ozone was produced. Observations were made from time to time of the odour in the room, and it was observed in a good many cases that the ozone odour gradually disappeared and the odour of the substance experimented upon returned. In some cases ozone was again generated until its odour was pronounced, and observations again made with reference to the disappearance of the ozone odour and the reappearance of the odour of the substance experimented upon. The conclusion was

drawn that the ozone did not destroy the substance giving the odour but masked it; this conclusion was based upon the disappearance of the ozone odour and the return of the other odour. No other evidence whatever on this point is presented.

In these experiments no attempt seems to have been made to determine the amounts of the odorous substances which were present in the air except by the odour. The experimenters apparently did not consider the fact that the odours of substances differ a great deal in intensity, and that the quantities of substances which would be present, even though the intensity of the odour was the same, would differ very much. These authors also failed to keep in mind that the destruction of odours by ozone is an oxidising process, and that this, as well as all chemical reactions, is quantitative in the sense that a definite amount of oxygen is required to oxidise a definite amount of an oxidisable substance.

The following reaction takes place when ozone oxidises hydrogen sulphide:—



—that is, 34 parts of hydrogen sulphide would require 48 parts of ozone for their oxidation. When the hydrogen sulphide is dissolved in water, the sulphur liberated is still further oxidised by the ozone to sulphuric acid, which would require a still larger quantity of ozone, but, according to the reaction given, a somewhat larger amount of ozone than hydrogen sulphide would be necessary for the destruction of this substance. Now, if the intensity of the ozone odour is much greater than that of the odour of hydrogen sulphide, the hydrogen sulphide would be oxidised by the ozone in the experiments reported by Jordan and Carlson and some other authors quoted, and the hydrogen sulphide odour would then return, as reported by these investigators.

In order to verify these conclusions, experiments were carried out to ascertain the amount of hydrogen sulphide which will give a distinct odour. A large balloon flask of 30 litres capacity was used. The hydrogen sulphide was produced by treating known weights of carefully analysed iron sulphide with dilute sulphuric acid. The reacting substances were placed on a watch crystal, suspended in the centre of the balloon flask. In addition to the odour, tests were made with lead acetate paper.

Intensity of Odour of Hydrogen Sulphide.

Mgrm. H ₂ S per cubic metre.	Test with lead acetate paper.	Odour.
977	Very black	Very strong
244	Very black	Strong
61	Very black	Distinct
30	Turned black slowly	Fairly distinct
15	Brown on edges	Faint
7.6	Turned brown very slowly	No odour

While to obtain a distinct odour of hydrogen sulphide 61 parts are required, the odour of ozone is very marked when present to the extent of 1 part per million, the limit being 1-10th part per million. In the experiments of Jordan and Carlson, the concentration of the hydrogen sulphide must have been from 30 to 60 mgrms. One part of ozone would have given a strong odour, which could mask the odour of the hydrogen sulphide until by the oxidation of the latter the ozone was decomposed. Less than 1 part per million of the hydrogen sulphide would be destroyed by this oxidation, leaving a sufficient amount of hydrogen sulphide to give a very distinct odour. On again generating ozone until a strong ozone odour was obtained, the hydrogen sulphide would be again "masked," and when the ozone odour had disappeared the hydrogen sulphide odour would reappear. This could be done repeatedly, as reported by Jordan and Carlson. The conclusion which they drew, however, is entirely unjustified, namely, that their experiments showed that the hydrogen sulphide odour was merely masked and hydrogen sulphide not oxidised or destroyed by the ozone.

* Read at the 6th Semi-annual Meeting of the American Institute of Chemical Engineers, Troy, New York. From the *Journal of Industrial and Engineering Chemistry*, vi., No. 8.

In order to verify this conclusion the following experiment was carried out:—A concentration of 25 mgrms. of hydrogen sulphide was treated with ozone of a concentration of 35.6 mgrms. per litre. In these concentrations there would be just enough ozone to oxidise the hydrogen sulphide. In this experiment the ozone odour was at first very pronounced, but after this odour had disappeared there was no hydrogen sulphide odour. A slight acidity was indicated by the reddening of blue litmus-paper. The ozone used had been very carefully tested for nitrous oxides, but none were found.

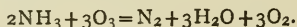
Another experiment was carried out in which the ozone concentration was 7.6 parts per million, while the hydrogen sulphide concentration was 60.7 mgrms. per cubic metre, so that only a small part of the hydrogen sulphide could be oxidised by the ozone present. At first only the odour of the ozone could be detected. The hydrogen sulphide odour gradually returned, so that within one hour a faint and after two hours a distinct hydrogen sulphide odour was detected, while the ozone odour had entirely disappeared.

This experiment could be repeated three or four times, as reported by Jordan and Carlson on page 33 of their article. They further state: "The mechanism of this masking action of ozone does not concern us here." If the authors had considered the "mechanism" of this action they might have reached entirely different conclusions, and would have seen that their experiments were in exact accordance with the theory that ozone oxidises hydrogen sulphide and other substances. They still further refer to the fatigue of the olfactory-end-organs by the ozone. They say, "Strong concentrations of ozone rapidly fatigue or anaesthetise the olfactory epithelium." One wonders why the authors did not make this statement general, and state what every chemist has frequently observed, that hydrogen sulphide and the numerous other odours which are present in chemical laboratories produce the same effect on olfactory epithelium, so that these odours are not noticed by workers in the laboratory.

Hydrogen sulphide is also oxidised by the air, as is shown by the fact that the odour slowly disappeared in a duplicate experiment in the absence of ozone.

In some cases ozone acts as a catalytic agent. This was shown by the action of ozone on linseed oil. Weighed quantities of linseed oil were exposed to air and ozone. The oil exposed to air gained 17 mgrms., while an equal quantity exposed to the action of ozone gained 110 mgrms. during the same time. The amount of ozone generated was 11.4. The ozone, therefore, acted as a catalytic agent, causing the absorption of 82 mgrms. of oxygen, which is nearly five times as much oxygen as was absorbed by the oil exposed to air alone. It is reasonable to suppose that ozone would act as a catalytic agent and cause the oxidation of other oils and organic substances similar to linseed oil.

In the case of ammonia the same considerations apply. Ammonia is oxidised by ozone in accordance with the following equation:—



In this case 1 part of ammonia is oxidised by about 4 parts of ozone. A study of the intensity of the odour of ammonia gave the following results:—

Intensity of the Odour of Ammonia.

Mgrm. NH ₃ per cubic metre.	Test with litmus paper.	Odour.
1000	Turns blue readily	Strong
659	Turns blue slowly	Fairly strong
329	Turns blue slowly	Fairly strong
165	Turns blue very slowly	Fairly strong
82	Turns blue very slowly	Quite distinct
41	Turns blue on edges very slowly	Faint
21	Turns partially blue on edges very slowly	Very faint
10	No action	No odour

Experiments were carried out in which known amount, of ammonia were treated with definite amounts of ozones and the ammonia remaining was determined by absorption with sulphuric acid and nesslerising. Ammonia is acted upon very slowly, so that twenty-four hours were allowed for the reaction. The concentration of the ozone was 35.6 mgrms., and of the ammonia 125 mgrms. per cubic metre. After twenty-four hours, 78 mgrms. of ammonia remained in the flask containing air and 75 mgrms. in the flask containing ozone. The quantity of ozone present was sufficient to oxidise 8½ mgrms. of ammonia per cubic metre. The experiment indicates some oxidation of ammonia by ozone. Erlandsen and Schwartz state that their results showed no action of ozone on ammonia (*Zeit. f. Hyg.*, 1913, p. 81).

Experiments were also carried out to ascertain the intensity of the odour of oil of cloves. It was found that 66 mgrms. per cubic metre would give a strong odour. The amount of ozone necessary to oxidise oil of cloves cannot be calculated exactly, but it would probably require several times more than an equal weight. On subjecting the oil of cloves vapour in a concentration of 36.6 mgrms. per cubic metre to the action of ozone of a concentration of 33 mgrms. per cubic metre, it was found that at first a distinct odour of ozone could be detected, which gradually disappeared, and was replaced by a sweet odour, which had no resemblance to the strong odour of the oil of cloves. Very evidently the oil of cloves, or one of its strong-smelling constituents, is oxidised, at least partially, so as to leave an organic compound having an entirely different odour. The flask was allowed to stand a total of twenty-one hours, although the reaction was practically complete within two to three hours. The reaction did not seem to be entirely regular. The experiment was repeated several times, and the formation of the sweet aromatic substance repeatedly observed, but at times the odour of cloves persisted. Any excess of ozone was removed by shaking with 10 per cent ferrous sulphate solution. Control experiments were also made with a balloon flask containing oil of cloves and air only. Erlandsen and Schwartz have made a similar observation with respect to skatol and indol. They state that these substances are completely decomposed by ozone with the formation of pleasant smelling substances similar to coumarin. They also state that mercaptan is rapidly decomposed by a large excess of ozone. These authors also found that hydrogen sulphide is oxidised by ozone. Jordan and Carlson also mention the work of Erlandsen and Schwartz, but state that the results of the latter agree with those of Jordan and Carlson in showing that ozone masks odours and does not oxidise the substances discussed. Jordan and Carlson even state that "the inability of ozone to oxidise (to any appreciable extent) ammonia vapour and oil of cloves is very striking." Franklin gives the results of experiments showing the oxidation of a great many organic substances, and demonstrated that carbon monoxide is oxidised to carbon dioxide (*Heating and Ventilating Magazine*, x., No. 11).

Undoubtedly many of the conflicting conclusions which have been reached are due to the failure of experimenters to take into account the quantitative relations between ozone and the substances to be oxidised, and have generally failed to realise that on account of the much greater intensity of the odour of ozone than that of other substances producing odour, far too little ozone has been employed in the experiments. The odour of ozone is at least 100 times as intense as that of other substances having a pronounced odour.

The common method of using ozone to destroy odours seems to be justified by these considerations. The ozone machines in good practice are operated so that a very small concentration of ozone in the air is produced. The continued renewal of this small amount of ozone oxidises the odorous substances, and gives the total quantity of ozone required by chemical theory.

Jordan and Carlson undertook to prove that ozone does not destroy smoke by coating a piece of glazed paper uni-

formly with a thin film of lampblack and subjecting the carbon to the action of ozone for ten hours, and state that there was no effect on the lampblack. They regard this as evidence that ozone does not destroy smoke, although they state that smoke also contains carbon monoxide, sulphurous acid, &c. They seem to have made no attempt to study the effect of ozone on carbon monoxide and sulphurous acid, but state that the assertion that "ozone destroys smoke" is equivalent to a deliberate deception, because ozone does not oxidise carbon particles suspended in the air. Not being chemists, Jordan and Carlson might not have known that carbon is extremely difficult to oxidise, but they should have known that carbon monoxide and sulphurous acid, as well as creosote and other pungent and aromatic organic substances present in smoke, produce disagreeable and toxic physiological effects. It is just these constituents of smoke which are easily oxidised by ozone. The carbon which is not acted upon is totally inert and harmless.

Jordan and Carlson also carried out investigations on the action of ozone on air bacteria. As has already been stated, their determinations of the concentration of ozone cannot be relied upon, because acidified solutions of potassium iodide were used, which give high results. The authors admit that the plate method which they used was not an exact one, and that, therefore, the results were irregular. They obtained a reduction of bacteria from 64 to 38, 49 to 18, 61 to 67 (increase), 78 to 34—that is, the bacteria were reduced to 40·6 per cent, 63·3 per cent, and 56·4 per cent in three tests, while in the fourth there was an increase to 109·8 per cent. Most authors would discard the fourth test, and consider the reduction to be about 55 per cent. Jordan and Carlson then tried Winslow's more exact method, but did not use a large enough sample for the test (4·5 litres), so that the highest number of bacteria counted was 7. It is not good practice in bacteriological work to rely on counts of so small a number. Jordan and Carlson draw the following strange conclusion from their results:—

"2. The alleged effect of ozone on the ordinary air bacteria, if it occurs at all, is slight and irregular even when amounts of ozone far beyond the limit of human physiological tolerance are employed."

There is no reason to suppose that the ozone used in these experiments was "far beyond the limit of human physiological tolerance." The reduction in the number of air bacteria is not "slight and irregular." The experimental results of Jordan and Carlson agree with the results obtained by one of us in New York school rooms, showing a reduction in air bacteria and moulds of 75 per cent, 91 per cent, and 91 per cent, the greater reduction resulting from longer exposure to ozone ("Purification of Air and Water by Means of Ozone," Olsen, Fourth International Congress of School Hygiene). No ill effects were observed on the children and adults present during these tests.

Jordan and Carlson (p. 34) state: "Some bacteria are undoubtedly killed by ozone, especially if they are in a moist condition." This statement is correct, as it is generally recognised that ozone destroys moist bacteria very rapidly. The conclusion drawn by Jordan and Carlson is very far from being correct. They say: "In practice, however, the fact is of very slight importance." The works of Chapin, Doty, and of Winslow and Robinson have fairly disproven the belief, held so long, that bacteria existed as a menace in rebreathed air. It has been shown that infection occurs but rarely from air-born bacteria, and then only when the bacteria are in the moist condition. It is just these virulent bacteria which are quickly destroyed by ozone even in low concentrations. The bacteria which resist the ozone are powerless to transmit disease.

It is by no means necessary to show that ozone is capable of sterilising the air in order to show that it is useful in ventilation. There is, in fact, no other disinfectant which can be used even in low concentrations in living rooms. All other known disinfectants are highly dangerous in concentrations high enough to be at all effective.

Ozone in low concentrations will both remove odours and will materially reduce the bacteria content of the air.

Jordan and Carlson attempted to show that ozone is dangerous by subjecting guinea-pigs to high concentrations until the animals died. They also forced strong ozone (10 parts per million) directly into the lungs of dogs and rabbits after performing tracheotomy under ether, and inserting a tube well below the larynx and treating the wound with cocaine. They say they did this because at least three-fourths of the ozone is decomposed by the mucous membrane of the respiratory passages. It is difficult to see what bearing this experiment can have on the use of ozone in ventilation. The ozone which was forced into the lungs must have been several hundred times as concentrated as it is ever used in ventilation. It would have been quite as logical to place animals in pure oxygen or even in an atmosphere of 50 per cent oxygen, and also force these gases directly into the lungs. When the animals died and the lungs were found to be inflamed, the conclusion might be drawn by highly academic experimenters that it is dangerous to breathe air containing 20 per cent oxygen.

Jordan and Carlson carried out experiments with what might be called low concentrations of ozone. They subjected 4 cats, 4 rabbits, 6 guinea-pigs, and 12 rats to ozone of 1 part per million nine hours daily during two weeks, so that irritation of the eyes and nose was produced. Body weight, appetite, and general condition were noted. No ill-effects on appetite and body weight or general condition could be observed. The conclusion could, therefore, be drawn that ozone in moderate concentrations is harmless, but Jordan and Carlson warn us that this conclusion is not justified.

They say: "We desire to state, however, that this test does not warrant the conclusion that the ozone in concentrations that may be used in practical ventilation is harmless to man. Two weeks is a short time in the life of a man. If ozone in ventilation should come into general use, it would mean in the case of office and shop workers exposure to ozone from six to ten hours a day six days of the week, from nine to twelve months of the year for from twenty to fifty years. And even if this prolonged exposure to ozone should prove harmless to the robust person, what about the unfortunate person whose lungs have only slight powers of resistance?"

Jordan and Carlson seem to have fallen into the error of assuming that because they have not tried to, and therefore have not demonstrated actually benefit from the use of ozone, this is equivalent to having demonstrated the reverse, i.e., the harmfulness of ozone.

If the facts presented in this paper are properly interpreted, they will be found to be in accordance with the view that ozone is a powerful disinfectant and deodorising substance, which in suitable concentration is without any injurious effects whatever. The elimination of odour is by no means the least important function of ozone, and there is no other agency available except dilution with fresh air. In many cases it is impossible to introduce enough air for this purpose without producing annoying and dangerous draughts of air, not to mention expense of blower installation and operation, as well as heating the air. As a matter of fact, before ozone was available disagreeable odours have often been considered unavoidable nuisances which could not be eliminated or overcome.

With reference to the alleged harmful effects of ozone, no single instance of harm to a person from the proper use of ozone in ventilation has been published, but all adverse opinions have been deduced, by inference, as in the paper by Jordan and Carlson, from experiments performed with very high concentrations, while all efforts to produce harm experimentally with weak ozone have failed.

Jordan and Carlson report that twenty-six animals, exposed for fourteen days, during nine hours each day, to concentrations high enough to cause irritation of the eyes and nose, suffered no ill effect whatever. Hill cites the

cases of the numerous workers in the London underground tubes, who have shown no ill effect in three years. Gminder cites the unharmed workers in the spinning mills at Reutlingen, and numerous similar instances of prolonged proper use of ozone without a single complaint are to-day in existence. The Jordan and Carlson report is the most elaborate and convincing laboratory test that has been published.

THE DETERMINATION OF MERCURIC IODIDE IN TABLETS.

By A. W. BENDER.

SOME difficulty was experienced by the writer in finding a method for the accurate determination of mercuric iodide in tablets, and having found one that gives very good results, it was thought that it might be of some interest to others engaged in analytical work.

The work was confined chiefly to the assay of tablet triturates (compressed), and the difficulty experienced was due, in a large measure, to the other ingredients in the tablets, namely, terra alba, potato starch, talc, and gelatin. Several methods and modifications of methods were tried on the tablets with very unsatisfactory results. It was then thought advisable to make a very accurate tablet granulation and to work on this known mixture until a suitable method for assay was found. The method which was finally found to give satisfactory results, both on the granulation and the tablets, is a modification of the sulphide method, the details of which will be given later.

The first method tried consisted of the use of potassium iodide solution for dissolving the mercuric iodide and the subsequent determination of mercury in the filtrate by evaporation to dryness with nitric acid and precipitation with hydrogen sulphide, but this was found to give very low results. Some modifications of this method were also found to give low results, due to the difficulty in filtering and washing the insoluble matter free from potassium mercuric iodide, and also to loss in the evaporation to dryness with nitric acid. In precipitation with hydrogen sulphide in a hydrochloric acid solution it was necessary to wash the precipitate with carbon disulphide. As the tablets showed only a very faint trace of iron, precipitation in ammoniacal solution was later used in this method and also in the modification of this method which was found to give accurate results.

Hunter's method for the determination of small amounts of iodine was suggested and tried with results that were also low, owing to the difficulty in fusing the mixture and dissolving the fusion.

Another method was tried which consisted in the use of an acid mixture for the solution of the mercuric iodide and the subsequent precipitation with H_2S in ammoniacal solution. This gave somewhat higher results but they were not uniform.

In making the tablet granulation a formula was used containing the ingredients mentioned above, which were known to be present in the tablets in question. Of the dried granulation 4.22 grms. represented one grain of mercuric iodide. This amount was taken for all of the assays on the granulation.

The method which was found to give accurate results is as follows:—

Powder a sufficient number of tablets to represent 1 to 2 grains of mercuric iodide. Place in a 180 cc. Erlenmeyer flask and add 20 cc. of 1:1 HCl. Add about 0.5 gm. $KClO_3$ and stopper with a glass tube reflux condenser. Digest on the sand bath until the mercuric iodide is all dissolved. Cool and dilute with water to about 100 cc. Wash glass tube condenser and remove. Blow out chlorine with a current of air. Filter and wash insoluble matter by decantation. Make filtrate alkaline with ammonia and precipitate immediately in the cold with a

slow stream of H_2S . Let stand for a few hours and filter through a weighed Gooch crucible. Wash with water and alcohol, dry at $100^\circ C$. and weigh. Grms. of $HgS \times 30.17 =$ grains of HgI_2 . Grms. of $HgS \div 1.955 =$ grms. of HgI_2 .

The results of the analytical work using this method are as follows:—

Tablet Granulation (Five Assays).

(4.22 grms. taken contained 1.0 grain HgI_2).

Grains HgI_2	..	..	1.11	1.08	1.04	1.12	1.03
----------------	----	----	------	------	------	------	------

Powdered Mercuric Iodide (Two Assays).

(0.1 gm. Sample).

Gm. HgI_2	..	..	..	0.1004	0.1024
-------------	----	----	----	--------	--------

Tablet Triturates $\frac{3}{16}$ th grain (Six Assays).

(Sample 30 Tablets).

Grains HgI_2	..	0.97	1.01	0.97	0.99	0.98	1.00
----------------	----	------	------	------	------	------	------

The method is simple and easy to manipulate and the results obtained were very satisfactory. It was also found to be useful for the assay of mercuric iodide and oleate of mercury.—*Journal of Industrial and Engineering Chemistry*, vi., No. 9.

A NEW METHOD FOR THE PRECISE STANDARDISATION OF HYDROCHLORIC ACID SOLUTIONS.

By LAUNCELOT W. ANDREWS.

WHEN the greatest precision is desired in standardising a volumetric solution, those methods should be avoided which (1) involve transferring or washing a precipitate; (2) depend upon the peculiarities of any particular indicator; (3) require the use of standard substances containing water of crystallisation, or those that may contain impurities difficult to detect—i.e., almost all organic compounds, or that cannot be positively dried without danger of decomposition; (4) demand any peculiarities of technique or any exercise of personal judgment that may make it difficult for different observers to obtain nearly identical results.

With these criteria in mind, I have devised and for several years used in practice a method the accuracy of which is only limited by the unavoidable errors of weighing. It depends upon the loss of weight caused by the replacement of NO_3 in silver nitrate by Cl. Since hydrochloric acid solutions kept in glass vessels always contain traces of chlorides and of other non-volatile impurities derived from the glass, the process must be so conducted as to avoid error from this source. The method is carried out as follows, when the solution to be standardised is 0.2/N:—

Select two porcelain, or, better, silica dishes, of approximately like size, form, and weight, of 75 to 100 cc. capacity, each being provided with a light watch glass or silica cover, and one of them with a silica or glass rod, short enough to lie under the cover. The dish without a rod will be referred to as the "companion dish." In the former, place 1.9 to 2.0 grms. of the purest silver nitrate. The absence of ammonium nitrate should be assured. Both dishes are put into an oven at 160° , the temperature raised to 240° , and kept there till the weight is constant. At this temperature no water is retained. After cooling in a desiccator, weigh both dishes, covered. Leaving both covers in the balance case, remove the dishes.

By means of a pipette, measure 50 cc. of 0.2/N hydrochloric acid, to be standardised, into the dish with the silver nitrate, using, of course, every precaution to make the measurement as accurate as possible, and noting the

temperature of the solution. At the same time, measure 50 cc. of the same acid into the companion dish.

Stir up the silver nitrate until all has dissolved and the silver chloride has clotted together, but do not remove the rod from the dish. Place both dishes in the steam bath at 95–100°, to evaporate the water without splattering, and finally dry at the temperature at which the silver nitrate was dried. Cool in the desiccator and weigh. The increase in the weight of the companion dish is assumed to represent the weight of non-volatile impurities contained in the acid, and its amount is subtracted, as a correction, from the observed weight of the silver chloride. This arrangement compensates for changes in the apparent weights due to atmospheric changes, so that, in case of very pure hydrochloric acid, the change of weight in the companion dish may be negative, a circumstance that need cause no apprehension.

By drying the silver nitrate, and, later, nitrate plus chloride, at the temperature of incipient fusion of the former, the same results are obtained as at 200° or 240°.

The normality of the solution is given by the expression

$$N = \frac{W - W_1 + w_1 - w}{0.02655 V}$$

in which

- V = Corrected volume of solution.
W = Weight in air of AgNO₃ + dish.
W₁ = Weight in air of AgCl + AgNO₃ + dish.
w = Weight of companion dish before.
w₁ = Weight of companion dish after.

In testing experimentally the precision of this standardising method, it was esteemed better to eliminate errors due to volumetric measurement of the solution, and to weigh the latter instead. Agreement of the results among one another will show whether any chlorine escapes or whether any other variable sources of error lie in the chemical reaction itself. The results of four such determinations follow. The weight of dish, cover, and rod was less than 70 grms.

Exp. A. Dish + AgNO₃ minus weight after = 0.5311 gm.
w₁ - w = 0.0001. Weight sol. 50.0445 gm.

Exp. B. Dish + AgNO₃ minus weight after = 0.5316 gm.
w₁ - w = 0.0004. Weight sol. 50.0548 gm.

Exp. C. Dish + AgNO₃ minus weight after = 0.53105 gm.
w₁ - w = 0.0001. Weight sol. 50.0391 gm.

Exp. D. Dish + AgNO₃ minus weight after = 0.5310 gm.
w₁ - w = 0.00005. Weight sol. 50.0396 gm.

Hence, the loss (corrected by companion dish) is respectively, per 50 grms. of solution taken: in A 0.53063, in B 0.53062, in C 0.53095, in D 0.53054. Since the balance was sensitive to only 0.05 mgrm. it is evident that errors of weighing alone account fully for the surprisingly small variations observed. It is, further, clear that these errors may be diminished, if there were any object in so doing, by operating with normal instead of 0.2N solutions. The disadvantage that the loss of weight is a smaller quantity than the absolute weight of the HCl determined, so that all errors are multiplied by the factor 1.37, is made unimportant by the great accuracy of the process in itself. In spite of its precision the method is not time-consuming, as the evaporations require no oversight. The time spent is practically only that required by the weighings. Most of this work was done in the laboratory of the Andrews Chemical Works, Davenport, Iowa. —*Journal of the American Chemical Society*, xxxvii, No. 10.

A Useful Laboratory Varnish.—This most useful applicant to metal and wood can be easily kept in the laboratory by making two solutions as nearly saturated as possible, one of vulcanised rubber naphtha, the other of pitch and bitumen in naphtha, and mixing when required. J. C. THOMLINSON.

A PRACTICAL METHOD FOR THE PREPARATION OF DRY STARCH, SOLUBLE IN COLD WATER, FOR USE AS AN INDICATOR.

By ROBERT M. CHAPIN.

WHEN, several years ago, the necessity arose for preparing a large quantity of dry starch which should be readily soluble in cold water and appropriate for use as an indicator in iodine titrations, no description of a sufficiently practical method of preparation could be found.

Wroblewski (*Ber.*, 1897, xxx., 2108) prepared the desired form of starch by running a concentrated solution of soluble starch, in a thin stream and with vigorous stirring, into a large excess of alcohol, followed by washing with absolute alcohol and ether, and drying *in vacuo*. He stated the resulting product to be soluble in cold water up to about 4 per cent, and to yield a pure blue with iodine. His original soluble starch was prepared by digesting rice starch with 1 per cent caustic potash solution.

In the present work Wroblewski's method of precipitation, &c., was found effective, but for the preparation of the original soluble starch Lintner's method of digestion with acid proved more satisfactory (*Journ. Prakt. Chem.*, 1886, xxxiv., 378). The first preparations, made in 1911, were of good quality, but were obtained through a series of tedious and expensive processes. Since that time, through the repeated preparation of large quantities of the material, the process has become so simplified and standardised that it is believed to be worthy of publication.

Into a 5 litre round flask with a long neck are brought 400 grms. potato starch, 2300 cc. distilled water, and, lastly, 80 cc. normal hydrochloric acid. The flask is well shaken, to wet and distribute the starch thoroughly, and is floated in a kettle of water previously brought to vigorous boiling. The neck of the flask rests conveniently on the side of the kettle at an angle of about 45°, and as soon as the flask is brought into the bath it is smoothly and continuously rotated about its longitudinal axis. As the flask becomes hot the starch forms an evenly distributed uniform jelly, which, in about seven minutes from the time of starting, begins to liquefy and to fall away from the wall of the flask. When this stage is reached the mouth of the flask is loosely closed with an inverted beaker and the flask left in the boiling bath, with an occasional rotation, until the mobile liquid shows no lumps of gelatinised starch remaining—one to one and a-half hours. The flask is then rapidly cooled in running water until it can be comfortably handled (about 50° C.), then methyl orange is added, followed by concentrated ammonia to alkaline reaction. Next is immediately added 800 cc. of 95 per cent alcohol, and, after thorough mixing and standing for a few minutes to allow air bubbles to separate, the liquid is strained through moderately coarse muslin. The addition of this proportion of alcohol notably reduces the viscosity, and increases the permanence of the solution. Starch will separate some time after the solution has become cold, but with proper management ample time remains for the subsequent operations. In fact, after experience has been gained, the amount of water, and in due ratio the total amount of alcohol, may be somewhat reduced. The solution, still at 40 to 45° C., is run through a number of fine jets into four litres of 95 per cent alcohol, with continuous stirring. The whole is left for at least forty-eight hours with an occasional thorough stirring after which most of the supernatant alcohol is decanted and the rest used to transfer the starch to a two-quart percolator provided with a filter-plate which is covered with filter-paper or cloth. Here it is percolated with 95 per cent alcohol, being stirred up with a stick at intervals to prevent the formation of clumps or fissures, until alcohol comes through the percolator of a specific gravity indicating a strength of 90 per cent. The starch is then transferred to a Buchner funnel, well drained with suction, and spread out to dry in a moderately warm place.

The resulting product is a fine white voluminous powder, more or less compacted to friable lumps which completely disintegrate under slight pressure. In less than a minute, a little of it thrown into cold water dissolves sufficiently to yield a good blue upon the addition of potassium iodide and iodine. Moistened with water or dilute alcohol, it becomes gummy and subsequently dries out to a horny mass, very slowly soluble in cold water. The efficiency of the preparation, therefore, resides largely in its fine state of sub-division and care must be taken during the process of preparation not to expose it to air until after thorough digestion with alcohol of 90 per cent strength. After drying it should be preserved from moist air, though it is not injured by exposure to ordinary atmospheric conditions.

The advantages of the material for iodide titrations made in the field with a portable outfit are sufficiently obvious. It is also a very convenient substance to have about a laboratory, although for highly accurate titrations it is somewhat inferior in sensitiveness and delicacy to a properly prepared fresh solution made from raw starch.

Since the above-described process was worked out, Fernbach has described very similar observations (*Original Communications, Eighth International Congress of Applied Chemistry, 1912, xiii., 131*); namely, that a dilute starch paste or solution run in a fine stream into a large excess of absolute alcohol or acetone, produces a finely-divided precipitate which is soluble in cold water. He apparently attributes the soluble qualities of the resulting product to the dehydrating action of the alcohol or acetone. Inasmuch as the horny form of precipitated starch previously mentioned, and indeed raw starch as well, becomes soluble in cold water when finely ground, the present writer believes that the prime factor which determines the readiness with which precipitated starch dissolves in water is simply the degree of fineness of its mechanical sub-division. It was early found that the more dilute the original starch solution and the greater the excess of alcohol, the finer, more voluminous, and more readily soluble in water became the resulting product, but naturally, the less practical became the process.—*Journal of Industrial and Engineering Chemistry, vi., No. 8.*

THE ANALYSIS OF A SAMPLE OF MONEL METAL.

In the course of preparing and analysing a series of alloys for the use of students of analytical chemistry, the writer examined a sample of Monel metal. As the particular combination of metals in that interesting substance is rather out of the ordinary, the method used is here described, in the hope that it may be useful.

Monel metal is described in a circular of the company producing it as having the following composition:—

	Per cent.
Nickel	67.00
Copper	27.00
Other metals (iron and manganese) ..	6.00
	100.00

For the analysis, half-grm. samples of fine chips were taken.

The sample is dissolved in as little dilute nitric acid as possible, and, after complete solution, about 5 cc. of concentrated sulphuric acid added, and the whole evaporated to copious fumes of sulphur trioxide. After cooling, the sulphates are taken up in water, the solution being diluted to about 100 cc. To this about 50 cc. of strong sulphurous acid solution is added, the whole heated, and about 2 grms. of KI, dissolved in a few cc. of water added. The whole is boiled for a few moments, when the white precipitate of

CuI should settle readily, and appear almost like a precipitate of AgCl. The solution should smell strongly of sulphur dioxide throughout the operation. The CuI, which should be perfectly white, is thrown upon a Gooch filter, which was prepared in the usual manner, washed with alcohol, then ether, and, after heating for twenty minutes at 105° C., weighed. The CuI is washed several times with dilute H₂SO₃, that solution being employed in transferring the precipitate from the beaker, then washed with a little alcohol, then with ether, and finally dried at 105° C. for twenty minutes, and weighed.

Weight of CuI $\times$ 0.3339 = wt. Cu.

$$\frac{\text{Wt. Cu}}{0.5} \times 100 = \text{per cent Cu.}$$

The filtrate from the copper is boiled thoroughly to remove all SO₂ and to concentrate it. To the hot solution is added about 1 gm. of ammonium persulphate, and then, slowly, dilute ammonia solution to alkalinity. The precipitate of ferric and manganic hydroxides is filtered off on a small paper, washed once with hot water, then is dissolved in hot dilute hydrochloric acid into a small beaker, and re-precipitated by ammonia and ammonium persulphate, the filtrate being added to the previous filtrate. The precipitate is burned in a platinum crucible, blasted, and weighed as Fe₂O₃ + Mn₂O₄. It is then fused with KHSO₄, the fusion extracted with water and dilute sulphuric acid, the ferric sulphate reduced by means of iron-free amalgamated zinc, and titrated in the cold with standard permanganate solution.

$$\text{Cc. KMnO}_4 \text{ sol.} \times \frac{\text{standard}}{0.5} \times 100 \dots = \text{per cent Fe}$$

$$\begin{aligned} \text{Wt. Fe} \times 1.4300 \dots &= \text{weight Fe}_2\text{O}_3 \\ \text{Wt. precipitate (Fe}_2\text{O}_3 + \text{Mn}_2\text{O}_4) - \text{Fe}_2\text{O}_3 &= \text{weight Mn}_2\text{O}_4 \\ \text{Mn}_2\text{O}_4 \times 0.7202 \dots &= \text{weight Mn} \\ \text{Wt. Mn} \times 100 \dots &= \text{per cent Mn} \end{aligned}$$

The combined filtrates from the iron and manganese contain all the nickel which is to be determined by the well-known dimethylglyoxime method. Inasmuch as the precipitate formed by this reagent is very bulky, the weight of nickel precipitated should not be more than 0.1 gm. for the sake of convenience in handling the precipitate. To this end the combined filtrates from the double precipitation of iron and manganese, after acidification with dilute hydrochloric acid, are made up to 1000 cc. in a standard measuring flask, and 250 cc. taken for each determination, care being taken that the temperature be constant. The acid solution, which represents one-fourth of the sample, is treated with an excess of a 6 per cent solution of dimethylglyoxime in absolute alcohol, and the whole raised to boiling. Ammonia is then added, with stirring, until the solution is just alkaline, the brilliant red precipitate of the nickel derivative of dimethylglyoxime appearing. The solution should be boiled a few moments, and a few drops of precipitant added to make sure of complete precipitation, when the precipitate is filtered out upon an 11 cm. hardened filter, and washed thoroughly with hot water. The precipitate prepared under these conditions filters and washes readily. It is now transferred by the aid of a very fine stream of water from the wash bottle, from the paper to a weighed platinum dish (the precipitate washing off the hardened paper very readily and completely), and the dish and contents placed on the water bath and heated to dryness. Drying is completed in the air bath at 100–105° C., and the whole weighed. This gives the weight of the precipitate (C₄H₇N₂O₂)₂Ni, which contains 20.31 per cent Ni.

$$\frac{\text{Wt. (C}_4\text{H}_7\text{N}_2\text{O}_2)_2\text{Ni} \times 0.2031 \times 4}{0.5} \times 100 = \text{per cent Ni}$$

The results of the writer's analysis, made rapidly, and

without any great effort to achieve extreme accuracy, follow:—

	Per cent.
Ni	26.95
Fe	3.00
Mn	2.95
Ni	66.94
Total	99.84

—*Chemical Engineer*, xix., No. 1.

PROCEEDINGS OF SOCIETIES.

ALCHEMICAL SOCIETY.

PRESIDENTIAL ADDRESS.

THE Fourteenth General Meeting of the Alchemical Society was held at 1, Piccadilly Place, W., on Friday, October 9, at 8.15 p.m., when the Honorary President, Prof. John Ferguson, LL.D., of Glasgow University, delivered his presidential address for the session, dealing with the book entitled "The Mirror of Alchemy."

The work, said Prof. Ferguson, a poem in two parts or seven books, appeared in London in 1654—5, in a small octavo volume. The authorship is usually ascribed to George Starkey, who is said to have been a native of Bermuda, a graduate in Arts, and a practitioner in medicine and pharmacy, though there is some doubt as to whether he really wrote it. The poem professes to give an insight into the mode of transmutation of "base" metals into silver and gold. The author first tries to prove that metals grow from seeds, and then relates some of his own experiences in Alchemy, following this up by a so-called "pedigree" of the metals. The second part of the book contains practical directions concerning furnaces and other apparatus, the materials to be employed, &c., under confused symbolic names, closing with a sort of recapitulation. But with all the helps possible, it is not easy to see how the multiplication of precious metal is effected, or even what is obtained. And the learned lecturer suggested that if the subject of the book were stated in the ordinary language of chemistry now, it would probably be found that all the reactions were familiar, that the gold apparently obtained was only the gold used in preparing the so-called "philosopher's stone," and that the deep enshrouding mystery was due to the want of the operator knowing what he was doing.

The meeting closed with a hearty vote of thanks to the Honorary President for so interesting a lecture. The full text of the lecture will be published in the October issue of the Society's Journal.

CORRESPONDENCE.

THE CAMBRIDGE SCIENTIFIC INSTRUMENT COMPANY, LIMITED.

To the Editor of the *Chemical News*.

SIR,—We should be obliged if you would draw the attention of your readers to the fact that we have taken over the business connection of the Leskole Company, Ltd., Palace Works, Enfield, who have gone into liquidation, also that Mr. F. Wakeham, the Assistant Manager of the Leskole Company, has joined our Staff.—I am, &c.,

F. WAKEHAM, Industrial Sales Manager.

October 13, 1914.

NOTICES OF BOOKS.

Principles of Metallurgy. By ARTHUR H. HIORNS. Second Edition. London: Macmillan and Co., Ltd. 1914.

THIS text-book of metallurgy gives a very concise account of the principles of the science, and descriptions of the methods of extracting all the more important metals from their ores. For students who have not time or opportunity to read widely in the journals of the various societies devoted to the study of metallurgy the comparatively short accounts of modern processes and plant will be valuable, and the chapters dealing with the properties of different kinds of fuels, fluxes, furnaces, &c., will probably be found particularly useful. The second edition has been considerably enlarged, and new material and illustrations have been added.

Elementary Household Chemistry. By JOHN FERGUSON SNELL. New York: The Macmillan Company. 1914.

THE student of home economics will find that this book contains a full and well-arranged account of the application of the principles of chemistry to household affairs. The elementary facts of chemistry, the laws of chemical combination, and the theories of the science are discussed, and many illustrative experiments are fully described. In these experiments substances which are met with in cooking and in domestic work generally are chiefly employed, and fuels, foods, and colouring matters are treated in some detail. The book puts before the student an enormous amount of information, and those who have no previous knowledge of chemistry will probably find it essential to work very slowly through it; otherwise the assimilation of anything like a fair proportion of the mass of facts it contains will be a matter of great difficulty.

Relative Effects of Carbon Monoxide on Small Animals. By GEORGE A. BURRELL, FRANK M. SEIBERT, and J. W. ROBERTSON. Washington: Government Printing Office. 1914.

THIS bulletin contains an account of an interesting series of experiments undertaken by the Bureau of Mines to determine the relative sensitiveness of birds and small animals to repeated exposures to atmospheres containing carbon monoxide. Canaries were found to be the least resistant to CO poisoning, and are therefore the most suitable for use in testing for vitiated air in mines. It is noteworthy that a man may feel distress in presence of 0.1 per cent of carbon monoxide, whereas animals appear unaffected in the same atmosphere. There is no decrease in susceptibility on the part of the animals after many exposures, provided that they are allowed to recover between exposures.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clix., No. 4, July 27, 1914.

Presence of Rare Earths in Scheelite.—Ch. de Rohden.—The author has examined the cathodic phosphorescence spectra of various specimens of scheelite, and has found that they all contain the rare elements, in very varying quantities in different scheelites. All the spectral phenomena observed could be explained as being due to known rare elements.

Hydrogenation under Ordinary Pressure of Aliphatic Ethylenic Compounds in presence of Nickel.—André Brochet and André Cabaret.—Compounds containing ethylenic bonds, such as cinnamic acid and its salts, can be hydrogenated in presence of nickel under atmospheric pressure. Cyclic compounds having an unsaturated lateral chain are also very readily hydrogenated. In the method of hydrogenation under moderate pressure ketones are converted into secondary alcohols, but at the ordinary pressure they are hydrogenated. This method of hydrogenation appears to be very uncertain, for with some substances it takes place very easily, while for no apparent reason it is very much slower with others.

Nitro and Amino Derivatives of Orthocyanophenol (Salicylic Nitrile).—MM. Cousin and Volmar.—When a mixture of equal weights of nitric and acetic acids is added gradually to a cooled solution of salicylic nitrile in acetic acid an energetic reaction occurs, and two mononitro-derivatives can thus be obtained. One is Meyer's com-

compound $\text{C}_6\text{H}_3\begin{matrix} \text{OH} & 1 \\ \diagup & \text{CN} \\ \text{NO}_2 & 5 \end{matrix}$, while the other is the 1.2.3-com-pound. By means of tin and hydrochloric acid each of these can be converted into the corresponding amino compound.

No. 5, August 3, 1914.

Quantitative Gravimetric Analysis of the Urea in Blood.—R. Fosse, A. Robyn, and F. Francois.—The amount of urea in blood can be determined by weighing its xanthylated derivative. The albuminoids of the serum are first removed by centrifugation with Tanret's reagent (mercuric chloride 2.71 grms., potassium iodide 7.2 grms., acetic acid 66.6 cc., water up to 100 cc.). An aliquot part of the liquid obtained is treated with an equal volume of acetic acid and 1/20 of the total volume of methyl xanthidrol is added. The crystals thus obtained are separated off, washed with alcohol, dried, and weighed. The urea corresponding to the aliquot part is equal to the weight of the urein divided by 7.

Bulletin de la Société Chimique de France.

Vol. xv-xvi., No. 13, 1914.

The Nickeling of Aluminium.—J. Canac and E. Tassilly.—An adherent layer of nickel can be directly deposited upon aluminium if the metal is previously washed with boiling potash solution, brushed with milk of lime, and then exposed to the action of a bath of potassium cyanide and of a ferruginous hydrochloric acid bath (water 500, HCl 500, Fe 1). After each operation the piece of metal must be washed with water. The nickeling-bath contains water 1000, nickel chloride 50, boric acid 20. The current density is 1 amp. per sq. cm., tension 2.5 volts. Nickelled aluminium can be employed for many purposes when a light unalterable and resistant metal is required.

Synthetic Preparation of Coal Gas.—Léo Vignon.—In presence of lime, water-vapour reacts with carbon to give hydrogen, methane, or ethylene, and thus a gas approaching coal-gas in properties can be prepared synthetically. Coal or coke can be used as the starting point. The volume of gas obtained is eight or ten times that obtained simply by distillation, and the greater part of the nitrogen in the coal is converted into ammonia. The gas is not toxic, the proportion of carbon monoxide being reducible to zero.

Cadmium Salicylate.—Oechsner der Coninck.—Cadmium salicylate can be prepared by treating freshly precipitated cadmium carbonate with an aqueous solution of pure salicylic acid containing a little alcohol. The salt thus obtained consists of tabular crystals, which can be dried at 95–96° for seven hours without undergoing decomposition. The formula of the salt is that of the monohydrated normal salicylate. It is only very slightly soluble in water at the ordinary temperature, rather more soluble in warm water, and readily soluble in boiling water. If the salt is heated with a slight excess of water at about

76–77° some salicylic acid is liberated, but the decomposition is only partial. At 165–167° the salt begins to give up CO_2 , a basic salt being formed. Above 170° it chars, and when calcined it leaves a dark brown residue containing $\text{CdO} + \text{CdCO}_3$.

Azomethines Derived from Phenylisoxazolone.—André Meyer.—Phenylisoxazolone condenses easily with aromatic parinitrosamines to give azomethines. Nitrosobenzene, however, will not condense. Phenyl isoxazolone also condenses with nitropyrzols or nitrosopyrazolones to give compounds to which the author has given the name "mixed rubazonic acids." In properties and formula they are analogous to Knorr's rubazonic acids.

Favourable Action of Manganese in Acetic Fermentation.—Gabriel Bertrand and Robert Sazerac.—The transformation of alcohol into acetic acid by *Bacterium aceti* is greatly accelerated by the addition of a certain proportion of manganese. The acceleration first increases with the proportion of the metal, passes through a maximum, and then decreases. These results indicate that the oxidasic role of manganese, already established in the case of the higher plants, also exists with the bacteriaciæ; that is to say, a group of plants the nutritive changes of which closely resemble those of animals.

Determination of Rhamnose in presence of other Methyl Pentoses.—Emile Votocek and R. Potmesil.—The formation of α -rhamnohexonic acid by the action of HCN upon rhamnose, and the oxidation of this acid by means of nitric acid are regular enough to be employed as the basis of a method of determining rhamnose. The final product, mucic acid, is obtained in the form of a crystalline precipitate. In presence of another methyl pentose the results are not so constant as those obtained with rhamnose alone, but they can still be employed, although not for the determination of small quantities of rhamnose in presence of a large excess of other sugars. The syrup to be analysed must, of course, contain only monosaccharides.

Atti della Reale Accademia dei Lincei.

Vol. xxiii. [i.], No. 11, 1914.

Palladous Salicylates.—G. A. Barbieri.—The author has investigated the question of the existence of a compound of palladium and salicylic acid analogous to that of copper, and has found that, by the action of potassium chloropalladite upon potassium salicylate in presence of K_2CO_3 , the compound $\text{Pd}\begin{matrix} \text{OC}_6\text{H}_4\text{COOK} \\ \text{OC}_6\text{H}_4\text{COOK} \end{matrix} \cdot 3\text{H}_2\text{O}$ is obtained, differing from the copper compound by one molecule of water. Sodium gives an analogous derivative. Palladous salicylic acid is precipitated by the addition of acetic acid to an alkaline palladous salicylate. If potassium palladous salicylate is added to a boiling solution of ammonium chloride an orange-yellow crystalline precipitate of $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ is formed.

MISCELLANEOUS.

Physical Society.—Sir J. J. Thomson, O.M., F.R.S., will deliver his Presidential Address to the Physical Society of London at the first meeting of the Society, on Friday, October 23. The subject of the address will be "Ionisation," and the meeting will be held at the Imperial College of Science, South Kensington.

Fish and Marine Animals as Sources of Oils.—In the second number of volume xii. of the "Bulletin of the Imperial Institute" there is a lengthy article on the utilisation of fish and marine animals as sources of oils, which is of special interest in view of the increased demand for fish oils to be hardened by hydrogenation for the purpose of making hard soaps. (See also the *Bulletin*, 1913, xi., 660). The tin resources of Malay and India are also exhaustively treated in the same number.

THE CHEMICAL NEWS.

VOL. CX., No. 2865.

MECHANICAL LIQUID FEEDER.

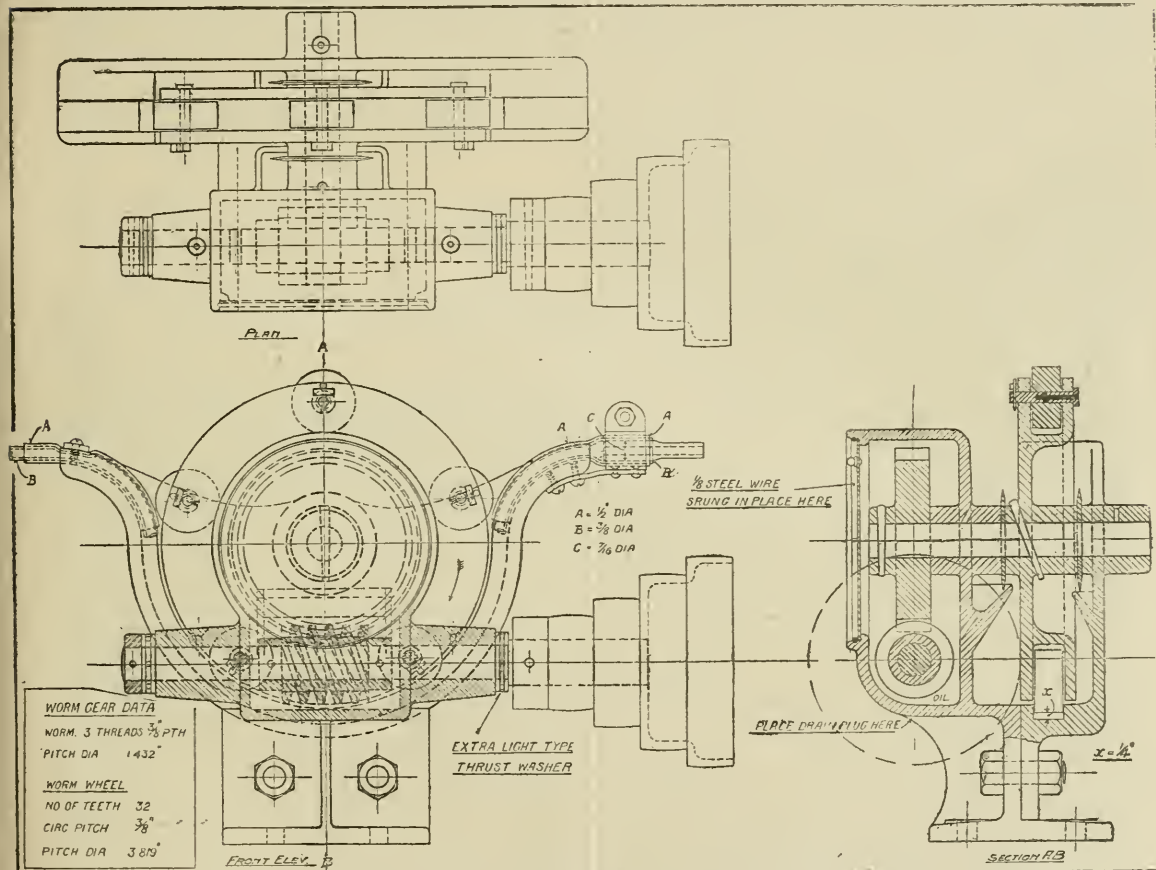
By F. H. LORING.

ENGINEERS, of course, know that, to perform an exceedingly simple mechanical act continuously, regularly, and in such manner as to be acceptable in widespread commercial practice, very considerable elaboration of device often becomes necessary. Such elaboration should

scum that may be present, especially when by accident the dregs of a tank get into the supply pipe. Moreover, the precision of the feed, which is under perfect manual control, is a great advantage. Syrupy liquids, as well as ordinary liquids, can be easily fed by this method under conditions of varying back-pressure or resistance.

A certain amount of mechanical elaboration, however, was found necessary to carry into practice this simple idea, and the working-drawing (quarter reduction from full size) here reproduced, shows this device which I have termed a *feeder*, as it is used for feeding liquids into specially-designed centrifugal machines. Referring to the *front elevation*, the worm and shaft-bearings are shown in superposed section. In the *plan* the rubber tubing and the clips are omitted, and the details of the foot part are not shown.

In the *section through A—B* a roller is outlined to show



be the means of ensuring a minimum of attention and trouble in the long run.

The problem of delivering small regulatable quantities of acidulated liquid day and night continuously without fail, and without variation due to careless manipulation or other causes, is not quite such an easy one as would appear upon first consideration.

After trying plunger-pumps which leaked and developed valve troubles, gravity-feeds with restriction tubes or taps, which clogged and were often wrongly adjusted notwithstanding indexes provided, to say nothing of breakages and sundry mishaps, I finally hit upon the simple scheme of pushing the liquid along by rolling a standard soft rubber tube. This method has the great advantage of not involving the use of a device which can become clogged or inoperative from a thickening of the liquid, or from any

the proper distance between the rollers and the bottom of the groove.

These feeders were originally tested by keeping them in more or less continuous operation day and night in different places for upwards of six months, and no trouble of any kind developed.

Step-pulleys are provided for four changes of speed, each step representing a known definite feed of liquid material through the tube. The other pulley, not shown in the drawing, is mounted on a light countershaft. Pure black commercial soft rubber tubing of best quality is employed, which remains in good condition for several months; should renewal be necessary, the cost is quite insignificant. The kneading action of the rollers does not appear to destroy the life of the rubber, and it is indeed surprising how many kinds of acids and corrosive salts in

solution may be pumped or fed by this device without causing appreciable deterioration of the rubber for at least a reasonable length of time. Of course some acids are destructive. These feeders are manufactured in considerable quantities, and may be purchased at reasonable prices on application to the writer.

30, Norfolk Street, Strand, London, W.C.

IS SILICA AN INDISPENSABLE CONSTITUENT OF PLANT FOOD?

By MARSHALL LUNDIE.

THE use of farmyard manure as a fertiliser was known to man long before letters existed by which it could be recorded. We begin to get records of some agricultural practices in Roman times. Even then not only the value of dung was known, but also the virtues of other manures, such as marl, were established. The great poet Virgil in his works makes reference to the fertilising effect of a crop of vetches, or lupins, upon the succeeding wheat crop. To whatever point the knowledge of manuring had reached in the time of the Romans, for a long time it made no progress. In the mediæval times agriculture took a step forward; the value of chalk, woollen rags, ashes was generally known. The experience of men of an enquiring turn of mind had built up a certain knowledge of manures and manuring, and had even begun to reason a little on the mode of action of these manures. In spite of the experience that was accumulating respecting the fertilising value of this or that substance, no real progress was made towards a theory of manuring until the beginning of the nineteenth century.

Before the development of the science of chemistry it was naturally impossible to form any idea as to how a plant came to grow, while the nature of the plant itself, of the air, water, and earth were equally unknown; no correct opinion could be reached as to how the latter gave rise to the former.

The true theory of the nutrition of plants begins soon after the discovery of the composition of the air. Priestley observed that plants possessed the power of purifying air rendered defective by combustion or by the respiration of animals, and he having been the discoverer of oxygen, it was found that the gas which leaves gave off was oxygen.

It was further demonstrated that light was essential for the development of these phenomena, while the oxygen was proved to be derived from the carbonic acid taken up, and that the gain in weight of the plant was practically represented by the carbon, combined with the elements of water, forming chiefly starch and sugar.

Such great scientists as Sir H. Davy, de Saussure, and Liebig took this important subject in hand, but it is to the latter that we must attribute the chief impulse which agricultural chemistry has received, for he drove home to the minds both of scientific men and of farmers the true theory of plant nutrition. He laid down the general principle that the carbon compounds, which constitute more than 95 per cent of the dry substance of most plants, are derived by the plants from the atmosphere, and that if the plant be supplied with the 2 per cent or so of mineral constituents which are found in the ash, it will then draw upon the atmosphere for all the materials the crop ultimately contains. These views of Liebig, coming at a time when great interest was directed towards agriculture, and backed by his great scientific reputation, aroused instant and widespread attention, being the foundation both of practical experiment and scientific research.

The ashes of a large number of plants were analysed, and the natural conclusion was drawn that all these ash constituents found were essential to plant growth, and were of equal importance. In the majority of cases the percentage of silica in the ashes was found to be very high, even amounting to as much as 50 and 60 per cent.

From this it was generally thought that silica was one of the chief constituents of plant food, and experiments were made using sodium silicate as a fertiliser, and the following, from A. D. Hall's "Fertilisers and Manures," p. 271, will show how far people went in drawing conclusions:—

"Silica is so large a constituent of the ash of many plants, particularly of the straw of cereals, that it was inevitably regarded as a necessary constituent of the food of such plants, and was naturally enough supposed to contribute to the stiffness of the straw. In his manure Liebig supplied the alkalis combined with silica, and when Way discovered that certain strata of the Upper Greensand, near Farnham, contained considerable quantities of silicates readily dissolved by acids, the rock was for a time extracted and ground up as manure for cereals."

Sir Humphry Davy's theory regarding the part that silica played in the plant was that it gave the plant a certain firmness, but he overlooked the fact that the leaves of the grasses which do not help to support the plant contain much more silica than the stems, and hence his theory cannot be correct.

This fact is also clearly brought out on glancing at the results of the analysis of the ashes of wheat given below.

	No. 1.	No. 2.	No. 3.	Average.
<i>Leaves.</i>				
Moisture (per cent) ..	9.49	8.92	11.82	10.08
Ash (per cent) ..	6.38	7.53	8.75	7.55
Silica (per cent) ..	1.088	1.369	1.18	1.212
<i>Stems.</i>				
Moisture (per cent) ..	13.36	10.47	14.17	12.66
Ash (per cent) ..	7.20	7.66	7.27	7.34
Silica (per cent) ..	0.46	0.143	0.744	0.449

At this time many exaggerated ideas were held as to the ammonia present in the atmosphere; the rain was believed to bring down as much as 30 to 40 lbs. per acre per annum of combined nitrogen instead of the 3 to 4 lbs. which we now know to represent the true quantity. This was due to imperfect methods of analysis. A great deal of controversy took place, some holding that it was unnecessary to use nitrogenous manures, as sufficient nitrogen as ammonia in the rain was supplied for the requirements of the plant.

The necessity of a supply of combined nitrogen was demonstrated experimentally, the yield being, in fact, roughly proportioned to the amount of combined nitrogen added as manure. If only the mineral constituents of the ash were supplied, the crop fell away rapidly as soon as the reserves of active nitrogen in the soil had become exhausted, and it was further demonstrated that the ordinary plants were incapable of utilising the full nitrogen of the air, but only took up nitrogen in a combined form from the soil as manure.

In addition to establishing the value of nitrogenous manures, experiments also settled in a practical fashion the question of which of the ash constituents were indispensable to the plant and were necessary constituents of a complete manure.

The fundamental necessity of phosphoric acid and potash, and the non-essential nature of soda, magnesia, and silica as manure constituents were soon established. The synthetical method of determining the character of the plant food was carried out first by Liebig by means of water cultures, with the result that the following nine substances were found to form the indispensable constituents of plant food, viz.:—

Acidic.	Neutral.	Basic.
Sulphur trioxide	Water	Potassic oxide
Phosphorus pentoxide		Magnesian oxide
Nitrogen pentoxide		Calcic oxide
Carbon dioxide		Ferric oxide

He further proved that each constituent of plant food performs certain definite functions in the system of the

plant, which cannot be performed by the other constituents.

It was at this time that Leibig enunciated the great Law of the Minimum, which states that if one of the necessary ingredients of plant food is provided in insufficient quantities, the plant takes up of the other necessary constituents only so much as is in a definite proportion to the quantity which is supplied in the minimum amount.

From these results it was clearly shown that silica, sodium, and chlorine were not indispensable, although it is a well established fact that barley, figs, and buckwheat thrive on a brack soil.

The author has carried out a series of water culture experiments with wheat, in order to demonstrate the non-essential nature of silica.

The experiment was carried out in the following manner:—A number of wheat grains were soaked over night, then put into a germinating dish (Professor Nobbe's apparatus) on May 31, 1911. It was observed on June 3 that they had commenced to germinate. Three of the most healthy were selected for the experiment. Nos. 1 and 2 were put into the water culture solution on June 8, while No. 3 was put in on the following day.

The water culture solution was made up as follows:—

In 1 litre of distilled water was dissolved—

1.0	gram.	of calcic nitrate
0.25	"	" potassic nitrate
0.25	"	" magnesian sulphate
0.25	"	" dihydric potassic phosphate
0.25	"	" ferric phosphate

By kind permission of Dr. Hahn these experiments were carried out in his greenhouse, where the plants were safely protected from the strong winds. On calm days they were put outside and exposed to the direct rays of sunlight.

The rate at which these young plants grew in the solution was very striking, no indication being given that they were sacrificing their health for height. It may be interesting here to give the measurements (in inches) of these young plants during the first few days of growth in the water culture solution to illustrate this rapid growth:—

	June 12.	13.	14.	15.	16.	17.	23.
No. 1 ..	4 $\frac{3}{4}$	5 $\frac{1}{2}$	6	7 $\frac{1}{2}$	8 $\frac{1}{2}$	8 $\frac{3}{4}$	12 $\frac{1}{2}$
No. 2 ..	4 $\frac{1}{2}$	5	6	7 $\frac{1}{2}$	8	8 $\frac{1}{2}$	12 $\frac{1}{2}$
No. 3 ..	2 $\frac{1}{2}$	2 $\frac{3}{4}$	3 $\frac{1}{2}$	4 $\frac{1}{2}$	5 $\frac{1}{2}$	5 $\frac{3}{4}$	10

The solutions had to be filled up every day with distilled water, owing to the transpiration current through the plant of water which enters by the root hairs, and is eventually evaporated from the leaves and other growing surfaces of the plant. This amount became considerable when the plant became full grown. On a warm day as much as 500 cc. was observed to be the decrease in volume of the culture solution. The solutions in which the young plants were growing were frequently shaken up so that more air, and hence oxygen, could be dissolved.

On July 12, August 26, September 9, September 29, October 12, fresh water culture solution was put in. These growing plants were carefully watched, and if at any time a fungus was noticed on the cork or cotton-wool, these would be immediately replaced by fresh sterilised material.

The height to which these plants grew, and the enormous number of stems and leaves produced in each case, were very striking—in fact, they looked more like bushes, and gave one the impression that they were making full use of the food material supplied, and were not sparing themselves in any way.

The plants, having come to perfection, were on October 20 removed from the solutions and hung up to dry. The heights they attained were as follows:—

	Height.	No. of ears of corn.
No. 1 ..	4 ft. 9 $\frac{1}{2}$ in.	24
No. 2 ..	4 " 7 $\frac{1}{2}$ "	16
No. 3 ..	4 " 2 $\frac{1}{2}$ "	24

When they were perfectly dry the stems and leaves of each were separately cut up and analysed as to the percentage of moisture, ash, and silica.

The total weight of dry straw (leaves and stems) was as follows:—

	Leaves.	Stems.	Total.
No. 1 ..	25.430 grms.	20.130 grms.	45.560 grms.
No. 2 ..	25.986 "	18.049 "	44.035 "
No. 3 ..	25.773 "	16.592 "	42.365 "

The average weight of one grain of wheat was found to be 0.447 grm., and this had increased on an average to 43.983 grms., excluding the weight of the roots and ears, which would have raised this figure still further.

The results of the analyses were as follows:—

	No. 1.	No. 2.	No. 3.	Average.
<i>Leaves.</i>				
Moisture, per cent ..	9.49	8.92	11.82	10.08
Ash, per cent ..	6.38	7.53	8.75	7.55
Silica, per cent ..	1.088	1.369	1.18	1.212
<i>Stems.</i>				
Moisture, per cent ..	13.36	10.47	14.17	12.66
Ash, per cent ..	7.20	7.66	7.27	7.34
Silica, per cent ..	0.46	1.143	0.744	0.449

Silica as it exists in sand and in rocks is virtually insoluble in pure water. It may be, as some botanists suppose, that plants exude from their root hairs some acid liquid which can extract and dissolve silica from rocky materials in the soil, and thus render it available for plant food.

We will now contrast this low percentage of silica in the leaves and stems of wheat grown in water culture solution with that of some crops grown on soil:—

Grasses.	Silica. Per cent.	Straw.	Silica. Per cent.
Meadow hay (first cut) ..	28.8	Wheat straw	67.6
Sweet grasses ..	36.5	Summer ..	47.6
Sour ..	33.2	Bran ..	71.7
Winter wheat (young plants)	42.2	Winter rye ..	56.3
Oats (young plants) ..	27.6	Summer rye	54.1
Maize (flowering plant) ..	18.3	Barley ..	52.0
		Oats ..	46.7

How different the demands for silica are in other crops may be shown by these figures:—

Buckwheat ..	5.5 per cent silica
Peas ..	6.8 "
Beans ..	7.3 "

Some of the seeds of these water cultures were put in a germinating dish, and after a few days were observed to germinate.

We have now completed the life cycle of one of these wheat plants, and have shown the non-essential part silica plays as a nutritive.

The silica is deposited in the cell membrane, and being in the epidermis of the plant supplies a certain protection from fungi (rust) sending its mycelium roots into the leaf.

I have it on Dr. Hahn's authority that a number of years ago a series of water culture experiments were being carried out at the South African College Chemical Laboratory, when they became attacked by rust, and in two days every plant was overrun with the fungus. This clearly shows that when the plant is deprived of its silica it can offer no resistance to the ravages of such pests as rust.

Here in South Africa we have a fine sunny climate, where everything thrives well, including the pests.

As to how and to what extent silica in a plant repels the attacks of fungoid growth is, indeed, a subject offering a wide field for research, and being of such great importance to us South Africans, surely this matter should be taken up and thoroughly investigated by our biologists.

It is well known that the silica in soils derived from

granitic rocks is less soluble than the silica which is derived from doleritic and basaltic rocks. In the granitic rocks the silica exists as pure quartz, and as trisilicate in feldspar and mica, whereas dolerite and basalt do not contain free quartz, and their constituent silicates like hornblende, augite, anorthite, are disilicates and monosilicates.

Since the silica in the granitic soils is less soluble than silica in the dolerite and basaltic soils, one cannot help thinking that the cereals which are such great silica eaters will take advantage of this when grown on doleritic or basaltic soils, and will contain more silica in the ashes than the cereals grown on granitic soils. If the theory is correct that the presence of silica in the cereals renders the plants more resisting to the attacks of fungoid growth, the cereals grown on dolerite and basaltic salts should suffer less than the cereals grown on granitic soils, provided that climatic and weather conditions are the same.

These are questions of such economic importance to South Africa that they should receive full attention at the hands of those who are carrying on research in connection with the production of cereals in our country.—*South African Journal of Science*, ix., No. 10.

THE DEHYDRATION AND RECOVERY OF SILICA IN ANALYSIS.

By F. A. GOOCH, F. C. RECKERT, and S. B. KUZIRIAN.

The Dehydration of Silica.

THE question as to the temperature which must be applied, and of the duration of the ignition necessary to bring silica to a constant weight in the analysis of silicates, has been the subject of much investigation and discussion. The opinion is general that in order to obtain the correct weight of anhydrous silica derived by precipitation in the usual course of analysis and ignition, the temperature employed must be that of the blast-lamp (Hillebrand, *Journ. Am. Chem. Soc.*, xxiv., 371; Treadwell, "Quant. Anal.," trans. Hall, 3rd ed., p. 486). Lunge and Milberg (*Zeit. Angew. Chem.*, 1897, p. 425) have shown, however, that silica obtained by hydrolysing silicon fluoride sustains after ignition in the full flame of a good Bunsen burner no further appreciable loss upon application of the blast heat, and these results have been confirmed by Löhöfer (*cf.* Hillebrand, *loc. cit.*) in Lunge's laboratory, and by Hillebrand, for silica thus derived from silicon fluoride. On the other hand, Hillebrand found in the case of silica derived by fusing quartz with sodium carbonate, treating the product with hydrochloric acid, and evaporating three times, with intermediate extractions and filtrations, that constant weights were obtainable only by blasting, and that blasting for half-an-hour (as is generally recommended) is often insufficient to secure constancy of weight. Quartz powder was used as the source of the silica in Hillebrand's experiments, and this was found to be 99.88 per cent pure, by careful treatment with sulphuric and hydrofluoric acids.

It has been shown recently in certain experiments by B. H. Walker and J. B. Wilson (U.S. Geol. Survey, *Circular No. 101*, August 16, 1912) that silica precipitated by acid may be brought to a constant weight by prolonged ignition over the Bunsen burner, thus avoiding the danger of loss which may occur when platinum is submitted to prolonged ignition with the blast-lamp. Three hours is the minimum period mentioned as requisite. It is to be noted, however, that in these experiments no test was made for impurity in the residue after ignition, and that, as will appear from the work to be described, the main source of trouble in bringing precipitated silica to a constant weight does not lie in the process of dehydration in ignition, but is due to the presence of an impurity which must either be volatilised or made to enter into stable chemical relation with the silica. From the results of certain experiments to be detailed it will appear that, while prolonged ignition

with the Bunsen burner or with the blast-lamp may sometimes be necessary to secure constant weights of silica separated from an alkali silicate by the action of hydrochloric acid, when the difficulty of securing constant weights appears it is to be attributed to the inclusion of foreign material more or less volatile and changeable at high heat, and not to the obstinate retention of water by the silica.

TABLE I.—Ignition of Commercial "Analysed" Silica.
Weight of SiO₂ found—

Hydrous silica taken (approximate weight). Grm.	After heating with the Bunsen burner in half-hour heats.					
	I. Grm.			After heating with the blast-lamp in fifteen minute heats.		
	I. Grm.	II. Grm.	A.	I. Grm.	II. Grm.	III. Grm.
0.2	0.1008	0.1006	0.1006	—	—	—
0.4	0.1930	0.1929	0.1926	—	—	—
0.4	0.1968	—	0.1967	0.1966	—	—
0.5	0.2501	—	0.2500	0.2500	—	—
1.0	0.4568	—	0.4568	0.4568	—	—
1.1	0.5343	—	0.5333	0.5330	0.5330	—
1.1	0.5309	0.5304	0.5306	0.5302	0.5302	—
1.1	0.5325	0.5327	0.5323	0.5324	—	—
1.1	0.5374	—	0.5372	0.5373	—	—
1.1	0.5392	—	0.5381	0.5381	—	—
1.1	0.5353	—	0.5351	0.5347	0.5347	—
			B.			
1.0	0.5464	0.5454	0.5447	0.5445	0.5444 (a)	—
1.0	0.5206	0.5204	0.5202	0.5202	0.5202	—
1.0	0.5447	0.5443	0.5441	0.5439	0.5439 (a)	—
1.0	0.5346	0.5346	0.5342	0.5342	0.5342	—
1.0	0.5427	0.5427	0.5427	0.5427	—	—
1.0	0.5376	0.5373	0.5373	0.5372	—	—
1.0	0.5511	0.5511	0.5511	0.5511	—	—
1.0	0.5445	0.5445	0.5444	0.5443	—	—
1.0	0.5344	0.5343	0.5340	0.5338	0.5338	—
1.0	0.5513	0.5513	0.5513	0.5512	—	—
1.0	0.5312	0.5312	0.5311	0.5311	—	—
1.0	0.5536	0.5536	0.5531	0.5531	—	—

(a) It was found that the crucible used in this determination was subject to loss when ignited by itself over the blast-lamp.

TABLE II.—Ignition of Silica separated by Acid after Fusion with Sodium Carbonate.

Residue of SiO ₂ after ignition with Bunsen burner.	Residue of SiO ₂ after subsequent ignition with blast-lamp.	Loss on ignition with the blast-lamp.	Na ₂ CO ₃ used in the fusion.	Residue after H ₂ SO ₄ +HF treatment, Na ₂ SO ₄ =Na ₂ O.	
Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
				A. — Residue dried at 110°.	
0.5300	0.5291	—	—	—	—
	0.5290	—	—	—	—
	0.5287	0.0013	4	0.0009	0.0004
0.5380	0.5373	—	—	—	—
	0.5368	—	—	—	—
	0.5365	—	—	—	—
	0.5363	—	—	—	—
	0.5363	0.0017	4	0.0010	0.0004
0.5365	0.5360	0.0005	4	0.0011	0.0004
0.4583	0.4575	0.0008	4	0.0014	0.0006
0.5071	0.5068	0.0003	4	0.0015	0.0006
0.5166	0.5159	0.0007	4	0.0012	0.0005

B.—Residue Dehydrated on Steam-bath and Heated with Acetic Anhydride.

0.1984	—	—	—	—	—
0.1980	—	—	—	—	—
0.4566 (a)	0.1977	0.0007	2	0.0016	0.0006
	0.4564	—	—	—	—
	0.4562	0.0004	4	0.0020	0.0008
	0.5322	—	—	—	—
	0.5325	—	—	—	—
	0.5325	0.0003	—	0.0010	0.0004

(a) Ignition extended to one hour.

TABLE III.—Recovery of Silica in Two Treatments.

Silica taken (grm.).			Silica recovered (grm.).								
After ignition with Bunsen burner half hour periods.	After ignition with blast lamp 15-min. periods.	Corrected for impurity (99.92 per cent pure).	First treatment.			Second treatment.			Total silica.		
			Ignited with Bunsen burner.	Ignited with blast lamp 15-min. periods.	Corrected by HF + H ₂ SO ₄ process.	Ignited with Bunsen burner.	Ignited with blast lamp 15-min. periods.	Corrected by HF + H ₂ SO ₄ .	Found.	Corrected for SiO ₂ in Na ₂ CO ₃ used (a).	Error.
<i>Desiccation at 110°.</i>											
A.											
0.5309	0.5306	0.5298	0.5300	0.5291	0.5281	0.0023	0.0023	0.0016	0.5297	0.5292	-0.0006
0.5304	0.5302			0.5290							
B.											
0.5215	0.5211	0.5207	0.5164	0.5161	0.5144	0.0077	0.0077	0.0071	0.5215	0.5211	+0.0004
0.5213	0.5211		0.5162	0.5160							
0.5456	0.5450	0.5444 (b)	0.5425	0.5420	0.5412	0.0057	0.0055	0.0048	0.5460	0.5456	+0.0012 (b)
0.5452	0.5448		0.5425	0.5418							
0.5355	0.5351	0.5347	0.5305	0.5295	0.5290	0.0050	0.0050	0.0049	0.5339	0.5335	-0.0012
	0.5351		0.5300	0.5293							
0.5436	0.5436	0.5432	0.5376	0.5370	0.5358	0.0080	0.0080	0.0072	0.5430	0.5426	-0.0006
0.5436	0.5436		0.5371	0.5365							
<i>Desiccation at 137° by Acetic Anhydride.</i>											
A.											
0.4568	0.4568	0.4563	0.4566	0.4564	0.4554	0.0008	0.0006	0.0004	0.4558	0.4553	-0.0010
	0.4568			0.4562							
B.											
0.5520	0.5520	0.5516	0.5460	0.5440	0.5438	0.0070	0.0068	0.0066	0.5504	0.5500	-0.0016
0.5520	0.5520		0.5460	0.5440							
0.5454	0.5453	0.5448	0.5403	0.5398	0.5390	0.0070	0.0065	0.0061	0.5451	0.5447	-0.0001
0.5454	0.5452		0.5401	0.5398							
0.5353	0.5349	0.5343		0.5396	0.5266	0.0075	0.0075	0.0072	0.5338	0.5334	-0.0009
0.5352	0.5347		0.5275	0.5270							
	0.5347		0.5272	0.5270	0.5453	0.0058	0.0056	0.0053	0.5506	0.5502	-0.0015
0.5522	0.5522	0.5465	0.5465	0.5460							
0.5522	0.5521	0.5517	0.5465	0.5459							

(a) 0.00013 SiO₂ in 1 grm. Na₂CO₃.

(b) It was found that the crucible used in the preliminary ignition was subject to loss on ignition over the blast-lamp.

The original material taken for our experiments was a commercial "analysed" hydrous silicic acid containing approximately from 45 to 50 per cent of anhydrous silica according to the degree of exposure. When digested with boiling water this material yielded traces of a soluble chloride and soluble sulphate. After the ignition of portions of the original substance—from 0.5 grm. to 5 grms.—for fifteen minutes over a large Bunsen burner, traces of chloride or sulphate could be still detected in the silica. When similar portions of the original substance were ignited over the burner for forty-five minutes or over the blast-lamp for half-an-hour neither chloride nor sulphate was found in the aqueous extraction of the residue, but treatment with sulphuric acid left a residue which amounted in the average to 0.24 per cent of the original substance. The barium sulphate precipitable by barium chloride from the solution of this residue proved to be nearly equivalent to the entire residue counted as sodium sulphate. Inasmuch as neither chloride nor sulphate could be found in this strongly ignited silica, it may be presumed that sodium oxide, remaining in combination with the silica, constituted, at least after the strong ignition, the impurity which after the treatment with the acids appeared in the form of sodium sulphate. Upon this presumption, the silica used was 99.92 per cent pure after the strong ignition. The record of experiments in which portions of the hydrous silica were heated during successive half-hour periods, with the

Bunsen burner and with the blast-lamp, is given in Table I. These results show plainly that the silica used may be brought to a practically constant weight in half-hour ignitions with a good sized Bunsen burner.

The next experiments show the effects of treating similarly the product obtained by fusion of the ignited silica with sodium carbonate, treatment with hydrochloric acid, evaporation, extraction with very dilute hydrochloric acid, and careful washing. In Series A of these experiments the drying was effected at 110° in the air-bath. In Series B the residue obtained by evaporation to apparent dryness on the steam-bath was moistened with acetic anhydride, and warmed over a radiator until this reagent fumed freely, the object of this treatment being to thoroughly desiccate the silica while preventing the otherwise possible formation of sodium silicate by action between silica, included sodium chloride, and water. Each of these methods of treatment leaves the silica drier, more porous, and therefore more effectively washable than is the case when drying is brought about by the steam-bath only. The results of these experiments are given in Table II. Every residue of silica was treated after the final ignition with sulphuric acid and hydrofluoric acid, the amount of sodium sulphate remaining was weighed, and the equivalent weight of the combined sodium oxide was calculated.

A comparison of these results with those of Hillebrand,

to which reference has been made above, points to the conclusion that the more perfect drying of the silica before attempting the process of extraction and washing results in smaller losses when the residue, which has been ignited over the Bunsen burner, is subjected to the heat of the blast-lamp. This fact suggests that the better desiccation is conducive to the more nearly complete washing of soluble material from the precipitated silica. At the best, however, the separation of foreign matter is not perfect, and the presence of material which is difficultly volatilised is sufficient to account for the slight changes in weight observed when the silica ignited with the Bunsen burner is submitted to further heating with the blast-flame. According to our experience, therefore, the difficulty in bringing to a constant weight the silica precipitated in the ordinary way, by the action of acid upon the products of fusion with an alkali carbonate, is not due to the obstinate retention of water but to the presence of foreign material difficultly volatile or slowly changeable at the temperature of ignition. In our experiments the foreign material retained in the precipitated silica must have been sodium chloride, and this in the process of ignition of hydrous silica is, as we have found experimentally, converted by the action of water to sodium oxide, which combines with the silica. In the experiments described above the sodium oxide retained by 0.5 gm. of silica amounted in the average to 0.0005 gm. After the treatment with sulphuric acid and hydrofluoric acid, the residue ignited at red heat is sodium sulphate, and from the weight found of this substance the equivalent weight of sodium oxide must be calculated in order that it may be used as the correction for the foreign material included in the silica as weighed. In the final ignition the use of the high heat of the blast-lamp is not advisable, lest the sodium sulphate lose weight and so vitiate the correction to be applied to the silica.

The Recovery of Silica after Fusion with Sodium Carbonate.

It is a generally recognised fact that, after fusion with sodium carbonate, silica cannot be recovered completely by a single filtration following any number of evaporations and treatments with hydrochloric acid (Hillebrand, *Am. Journ. Sci.*, xxxiv., 366; Treadwell, *loc. cit.*). To secure satisfactory results it is necessary to evaporate the filtrate after the removal of the main amount of silica by the first treatment, treat the residue with hydrochloric acid, and again filter.

The experiments detailed in Table III. record the results obtained in recovering silica by two such treatments after fusion with 3 grms. of sodium carbonate. The fused mass was treated with hydrochloric acid; the liquid was evaporated on the steam-bath; the residue, desiccated either at 110° in the air-bath or by the treatment with acetic anhydride, according to the method and for the purpose, previously described, was extracted with hydrochloric acid; the insoluble silica was filtered off, washed, ignited, and weighed; the filtrate from the silica insoluble in this first operation was evaporated, and the residue obtained was treated like the first residue.

In these experiments the deficiency in silica found after the first thorough evaporation and desiccation at 110° amounts in the average to 0.0051 gm., after correcting for silica introduced in the sodium carbonate, and this is practically the amount of silica recovered in the second treatment. In the experiments in which acetic anhydride (boiling-point, 137°) was used to moisten the residue (after thorough desiccation on the steam-bath) and then partially removed by boiling, the average deficiency in silica after the first treatment amounted to 0.0061 gm., and the amount recovered in the second treatment to 0.0051 gm. Obviously, the insolubility of the silica, after the process of desiccation, extraction, and filtration, depends very largely upon the thoroughness of the drying, and, while the drying at 110° or at 137° (in acetic anhydride) greatly diminishes the solubility of the silica as compared with that of the substance when simply dried on the steam-bath,

the treatment with acetic anhydride offers no advantage over the process of drying in the air-bath at 110°, at least when the contaminating substance is sodium chloride.

The slight variations in the weights obtained when residues which had been ignited with the Bunsen burner were submitted to the temperature of the blast-lamp appear to be due to the presence of sodium chloride, which by strong ignition is either transformed to sodium silicate or is partially volatilised.—*American Journal of Science*, xxxvi, p. 598.

TERBIUM.

By C. JAMES and D. W. BISSEL.

THIS element was first described by Mosander during his researches upon yttria, just previous to 1843, under the name of erbium. He stated that the oxide was orange-yellow and the salts colourless.

Later, several chemists, employing the fusion of the nitrate method, failed to obtain the original erbium of Mosander, so the name erbium was given to terbium, which gave a rose-coloured oxide.

Delafontaine maintained the existence of old erbium, or terbium as it was now called. He recommended samarskite (*Ann. Chim. Phys.*, 1887, xiv., 238) as a source of terbium, and described the preparation of a terbia of a dark orange-yellow colour. The salts prepared from it were said to be colourless and to show only a trace of the absorption of didymium.

Marignac (*Ann. Chim. Phys.*, 1887, xiv., 247) fractionated 300 grms. of gadolinite earths and obtained three sets of oxides: white yttria, rose erbia, and intermediate oxides of a more or less deep yellow colour. He separated the didymium from these and showed that the colour must be due to a third gadolinite oxide originally mentioned by Mosander and later denied by Bunsen and Bahr, and Cleve and Hoglund. Marignac's terbia, purified by the potassium sulphate method and the oxalic acid method, consisted of a dark orange-yellow powder.

Cleve confirms Marignac's conclusions with regard to the existence of terbia (*Bull. Soc. Chim.*, 1879, xxxi., 195).

Lecoq de Boisbaudran pointed out the complicated nature of terbium oxide (*Comptes Rendus*, 1886, cii., 153). He said that it contained variable proportions of yttria, holmia, ytterbia, samaria, erbia, and the yellow earth. Such material was submitted to many fractionations. The resulting products when tested by the spectroscope showed the possibility of the existence of three terbiums, which he designated by Za, Zβ, and Zγ. Zβ gave a very deep reddish brown terbia. The solution of the chloride gave only a weak absorption spectrum composed of the bands of dysprosium and of a band which appeared to belong to a new element. The same band (λ 487.7) appeared as strongly in the paler coloured terbias, and he, therefore, concluded that it was due to another terbia which he provisionally named Zδ. He was unable to fractionate further, since all the material was used up.

Boisbaudran examined a sample of impure mosandria, and found that it consisted of yttrium a and terbia as Marignac had supposed (*Comptes Rendus*, 1886, cii., 647).

Hoffmann and Kruss showed that terbia (of this date, 1893), which cannot be split up further by means of the double sulphate or formate methods, may be fractionated by solution in aniline chloride (*Zeit. Anorg. Chem.*, 1893, iv., 27).

Marc worked upon terbium material, obtained by Weiss during the preparation of didymium from monazite by the chromic acid method of Muthmann and Bohm, and came to the conclusion that, although his terbia was coloured deep brown, only a few per cent of the element causing this was present (*Ber.*, 1902, xxxv., 389). He also said that the solution of the oxide gave an absorption band λ 464—461.

Emma Portratz, in a paper on terbium and some of its compounds, describes the oxide as being of a brownish orange colour like some varieties of ochre (CHEM. NEWS, 1905, xcii., 3).

Feit worked on the yttrium earths from monazite and obtained a crude oxide, which he supposed contained about 12 per cent of terbia (*Zeit. Anorg. Chem.*, 1905, xliii., 267).

Urbain, by three different methods of fractionation, obtained a dark coloured earth between gadolinium and dysprosium, whose solutions showed the absorption band $\lambda 488$ (*Comptes Rendus*, 1904, cxxxix., No. 19). He kept, provisionally, the name $Z\delta$, given by Boisbaudran to the element possessing this property. The results of Marc were not duplicated. The latter stated that the salts of terbium possessed a pink colour, while Urbain showed that a common coloured impurity of terbium was dysprosium. The compounds of this latter element communicate a green tint to those of terbium. Urbain obtained about 100 grms. of the crude dark oxides. This material was submitted to a further long and careful fractionation, which gave 7 grms. of an oxide, that could not be divided by continued fractionation (*Comptes Rendus*, 1905, cxli., No. 12). It gave a dark brown oxide by ignition of the oxalate, and a black oxide when the sulphate was calcined at 1600° . The oxide corresponded to the formula Tb_4O_7 . The solution of this oxide showed the absorption spectrum of $Z\delta$, the inverse spectrum of $Z\beta$, the spark spectrum of Demarcay's I, and the phosphorescent spectrum of a meta element of yttrium and to $G\beta$ (Crookes). The atomic weight was found to be 159.22.

Urbain states that Boisbaudran's Za is identical with dysprosium (*Comptes Rendus*, 1906, cxliii., 229).

Urbain and Jantsch, in describing some new compounds of terbium and dysprosium, state that terbium can be weighed as the oxide Tb_4O_7 if it has not been heated to too high a temperature (*Comptes Rendus*, 1908, cxlvi., 127).

Urbain concludes among other things that the elements Γ of Demarcay, $Z\beta$ and $Z\delta$ of Lecoq de Boisbaudran, $G\beta$, ionium, and incognitum of Sir William Crookes are identical with terbium (CHEM. NEWS, 1909, c., 73).

Welsbach fractionating the yttrium earths by means of the double oxalates with ammonium oxalate, observed that terbium was distributed between the gadolinium and dysprosium fractions (*Chem. Ztg.*, xxxv., 658). He said that the separation was tedious, but might be carried out satisfactorily. On each side of the terbium the fractions were coloured deep ochre; also they gave no optical test for terbium. From this he concluded that old terbia consisted of three elements, which he provisionally named $TbI.$, $TbII.$, and $TbIII.$ $TbI.$ was closely related to gadolinium, and $TbIII.$ to dysprosium.

Separation.—The methods used originally gave an oxide containing only a few per cent of terbium oxide. These processes include: fusion of the nitrates; precipitation by potassium sulphate; precipitation of oxalates from a strongly nitric acid solution; the formic acid method.

When the nitrates are partially decomposed by heat, poured into water, boiled until clear and allowed to cool and crystallise, the least basic element separates first in the form of a crystalline basic nitrate. This method is not to be recommended for the extraction of terbium.

Terbium potassium sulphate and terbium sodium sulphate are very much less soluble than the corresponding double sulphates of yttrium and erbium, &c. They are more soluble than those of the cerium metals. Owing to the similar solubilities of the double sulphates of gadolinium and dysprosium, and also to the fractional precipitation nature of the method, it is very tedious.

The fractional precipitation of the oxalate from a highly acid solution of the nitrate is practically useless.

Terbium formate is very much less soluble than yttrium formate, and the formates might be used for the separation of yttrium and terbium, if it were not for the fact that they

form a double compound. Philippium formate was found to be yttrium terbium formate.

Later, Boisbaudran recommended the use of very dilute ammonium hydroxide. Urbain says this method is very tedious. He advises the following: fractional crystallisation of the double nitrates with nickel; fractional crystallisation of the simple nitrates in the presence of bismuth nitrate; fractional crystallisation of the ethyl-sulphates.

The double nickel nitrate method gave gadolinium nickel nitrate, in a very pure state, as the least soluble portion (Urbain, *Comptes Rendus*, 1904, cxxxix., No. 19). The most soluble fractions gave very dark coloured oxides, whose solutions showed a strong spectrum of dysprosium, a feeble spectrum of holmium, and an almost imperceptible band of $Z\delta$. These solutions possessed an olive colour. The middle fractions gave oxides, paler in colour, and the solutions when examined by the spectroscope revealed only the band belonging to $Z\delta$.

The Fractionation of the Simple Nitrates in the presence of Bismuth Nitrate.—Urbain found the solubility of bismuth nitrate in nitric acid to be greater than the solubility of gadolinium nitrate, but less than that of dysprosium. Since bismuth nitrate is isomorphous with the nitrates of the rare earths, it would accumulate with the terbium and enlarge the amount of material, thus making it easier to carry on the fractionation. The above chemist found, after a careful study, that bismuth nitrate is less soluble than the nitrate of terbium. However, he was unable to separate quantitatively terbium from gadolinium, as he had done with europium and samarium by the addition of bismuth magnesium nitrate. Bismuth was separated from the terbium fractions by means of hydrogen sulphide. The terbium was then precipitated by the addition of a solution of oxalic acid.

Fractionation of the ethyl sulphates rapidly separates terbium from most of the yttrium earths. This method has been extensively used by Urbain and Lacombe.

The authors, after due consideration, came to the conclusion that the only methods worth trying were the last three. The double nickel nitrate method must be a very good one, since, by it, Urbain obtained a pure white gadolinia. This process was tried, and some difficulty was encountered in the crystallisations. It requires considerable experience in order to get good crystals. It is also unfortunate that the liquid is so highly coloured, for it prevents observations being made with regard to changes in colour of the earth solutions themselves. In addition the absorption spectra cannot be studied.

The crystallisation of the simple nitrates was not tried, since it does not work anything like as rapidly as the bromate method. The ethyl sulphates are useful. It is a very great pity that they are so readily hydrolysed.

The material for the extraction of terbium oxide consisted of gadolinium oxide containing terbium oxide. There were also present certain amounts of dysprosium and holmium oxides and traces of those of yttrium and erbium. The whole was converted into bromates by warming with bromic acid. The bromates so obtained were submitted to a long and careful fractionation.

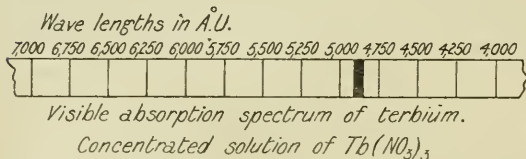
After a few series of operations, the whole of the terbium and most of the holmium and dysprosium were found to be in the most soluble portion. As the work proceeded, a faint absorption band appeared in the blue, when the least soluble fraction was examined by means of the spectroscope. This was due to small amounts of europium, which showed that europium bromate was less soluble than gadolinium bromate.

Europium bromate would, therefore, appear to possess the lowest solubility of all the rare earth bromates. The solubility first of all decreases as we go up the series in the following order: lanthanum, cerium, praseodymium, neodymium, samarium, europium. After europium has been reached, the solubility commences to increase again in this manner: europium, gadolinium, terbium, dyspro-

sium, holmium, yttrium, erbium, thulium, ytterbium, lutecium, celtium, and scandium.

By the time a considerable number of series of operations had been carried out, the colours of the oxides of the fractions were observed to show very much light upon the rapidity of fractionation. The least soluble—gadolinium bromate—gave a nearly white oxide. All gadolinium was removed from the series as soon as it gave an almost white oxide. With increase of solubility the colour of the oxides rapidly changes. They became darker and darker until a maximum was reached, after which the colours became paler. The most soluble fractions gave a buff coloured oxide. These portions were removed when this condition had been attained. From these results it can be seen that terbium is rapidly separated from gadolinium by means of the bromate method. The separation of terbium from dysprosium is not as simple as in the case of the previous element. Perhaps the ethyl sulphates would be the best salts to use for this portion of the work. The results of the application of this method will be described later on.

The fractions that gave the darkest coloured oxides showed only one absorption band—that of Z₈ or terbium. The more soluble portions of the terbium showed the absorption bands of dysprosium in addition, while the less soluble portions gave very faint neodymium bands, the latter indicating the fact that neodymium bromate comes between the bromates of terbium and gadolinium. It would, therefore, be reasonable to conclude that by the careful use of neodymium the separation of terbium and gadolinium could be carried out quantitatively. Neodymium can, of course, be readily separated from terbium



by many well-known methods, such as by crystallising the double magnesium nitrates with bismuth magnesium nitrate. Only three or four operations are necessary. Neodymium magnesium nitrate passes into the least soluble fractions, since it is practically insoluble in bismuth magnesium nitrate. The bismuth magnesium compound comes next, while the terbium magnesium nitrate collects in the mother-liquor.

A statement, made somewhat recently, by another worker with regard to the bromate method, led one to understand that there was considerable difficulty in separating yttrium from gadolinium. Yttrium bromate comes between the bromates of erbium and holmium with regard to their solubilities. It will, therefore, naturally tend to divide itself into two portions, one accompanying the erbium and the other the holmium and dysprosium. Therefore as soon as a fraction, less soluble than dysprosium, no longer gives the dysprosium absorption spectrum, it is free from yttrium. Since, in addition, terbium and neodymium come between dysprosium and gadolinium, the separation of yttrium and gadolinium must be extremely good. When we have a fraction containing yttrium more soluble than holmium and free from the absorption bands of this element, it is free from gadolinium.

The original bromates used in this work comprised many kilograms. As large amounts of gadolinium bromate were, however, rapidly removed from one end, and fair quantities of the bromates of erbium, yttrium, holmium, and dysprosium from the other, the bulk of material undergoing fractionation quickly decreased. The whole of the erbium was removed in the most soluble portion after a few crystallisations. This was followed by yttrium and holmium with some dysprosium. Finally the holmium

bands became very faint, and later dysprosium, with a little terbium, formed the most soluble fractions of the series.

By this time the fractions had become reduced to about 10 grms. in each. About 30 grms. of very pure terbium oxalate, giving a black oxide, were obtained. Thirty grms. of an oxalate not quite so pure were also separated.

The crystallisation of the chlorides from hydrochloric acid was used in the endeavour to separate small amounts of terbium from dysprosium. The chlorides formed very nice crystals, and the mother-liquor could easily be drained off. The rate of fractionation seemed to be about the same as in the case of the nitrates. The oxide from the least soluble was darker than that from the most soluble portion. This showed that terbium chloride like terbium nitrate passed into the least soluble fractions.

When a mixture of gas and air was directed upon terbium peroxide, or upon gadolinium oxide containing terbium peroxide, heated almost to redness, the mass immediately became incandescent and the gas usually took fire.

A strong solution of terbium nitrate gave an absorption spectrum consisting of one band in the blue as shown in the figure.

The authors conclude from their results that there is only one terbium. By means of the bromate process, terbium is comparatively rapidly separated from gadolinium; and neodymium, if present, comes between the two. This work agrees with that of Urbain and not with that of von Welsbach.—*Journal of the American Chemical Society*, xxxvi., No. 10.

A METHOD FOR THE ESTIMATION OF PODOPHYLLUM RESIN.

By W. M. JENKINS.

It seems to be a generally acknowledged fact that the therapeutic activity of podophyllum is due to the resin which it contains. While this resin is recognised in the United States Pharmacopœia, and its properties and solubilities are well described, it must be remembered that the resin is not a simple substance but a mixture of substances, the most important of which is a crystalline body called podophyllotoxin. From a therapeutic standpoint, however, podophyllum resin U.S.P. is a well known substance, and the dose is well defined. It would seem, therefore, that any attempts at assaying or standardising the drug should be in terms of podophyllum resin U.S.P. It was with this idea in view that the work described in this paper was undertaken.

All previous methods for the determination of podophyllum resin have been based on the idea that the resin is insoluble in water, and that by pouring an alcoholic solution of the resin into a large volume of acidulated water the resin would be completely precipitated, and could be collected and weighed (*Chem. Soc. Trans.*, 1898, p. 209). Through long experience with this precipitation method, however, it has been found that the results are very unreliable, and greatly affected by the conditions of the method, viz., the volume and temperature of the acidulated water, the amount of alcohol used, and the amount of sample taken. The only way to get results which were at all concordant was to adhere strictly to the same amounts of alcohol, water, acid, and sample; the results were thus purely arbitrary.

The reason for these variable results was later found to be the fact that podophyllum resin is slightly soluble in water, and that this solubility is increased by small percentages of alcohol, and hence the recovery of the full amount of resin by the precipitation method is impossible. Thus it was found that by dissolving 0.4 gm. of U.S.P. podophyllum resin in 10 cc. of alcohol, and precipitating the resin in 600 cc. of water acidulated with 10 cc. of

hydrochloric acid, only 75 per cent. of the resin was recovered.

Podophyllum resin is only partly soluble in chloroform, but is readily soluble in a mixture of 1 part of alcohol and 2 parts of chloroform. Hence it was thought that a mixture of alcohol and chloroform might be used for extracting the resin quantitatively from an alcohol solution which had been diluted with water.

When equal volumes of alcohol, chloroform, and water are mixed, this mixture separates on standing into two layers, the upper portion consisting approximately of 1 part of alcohol and 2 parts of water, and the lower layer of 1 part of alcohol and 2 parts of chloroform.

By keeping the proportions of alcohol, chloroform, and water constant, it was found that over 99 per cent of resin was recovered by three extractions with the alcohol-chloroform mixture when working with U.S.P. podophyllum resin.

When this method was applied to the fluid extract, however, and the resulting resin compared with the U.S.P. podophyllum resin, it was found to be darker, more hygroscopic, less soluble in alcohol and more soluble in water. Thus it was necessary to modify the method in some way, in order to obtain a resin identical with the official resin. This was accomplished by washing the alcohol-chloroform extract with acidulated water. The resin obtained by this modification was found to conform to the U.S.P. requirements for podophyllum resin, viz. :—

Soluble in alcohol in all proportions.
86.4 per cent soluble in ether.
69.1 per cent soluble in chloroform.
21.3 per cent soluble in boiling water.
0.1 per cent ash.

By this procedure, from 0.4 gm. podophyllum resin U.S.P. dissolved in alcohol 0.394 gm. was recovered, corresponding to 98.4 per cent.

Accordingly, the following method for estimating the amount of podophyllum resin in fluid extract podophyllum is suggested,

Measure 5 cc. of fluid extract podophyllum into a separatory funnel, add 5 cc. of alcohol, 10 cc. of chloroform, and 10 cc. of acidulated water containing 0.6 per cent hydrochloric acid (2 cc. HCl in 100 cc. water). Shake and allow the mixture to separate. Draw off the lower layer into another separatory funnel. Repeat the extraction twice, using 15 cc. of a mixture of 1 part of alcohol and 2 parts of chloroform each time, and add these extractions to the first. Shake the combined extractions with 10 cc. of the acidulated water, and allow the mixture to separate. Draw off the lower layer into a tared flask, and repeat the extraction twice, using 15 cc. of the alcohol-chloroform mixture each time. Evaporate the combined extractions and dry the residue to constant weight at 100° C.

For comparison a number of fluid extracts were assayed by this method, and, by the usual precipitation method, with the following results :—

Resin in Fluid Extracts.

Precipitation method.		Shake-out method.	
G. in 10 cc.	Per cent.	G. in 5 cc.	Per cent.
1. 0.424	4.2	0.3480	6.9
2. 0.420	4.2	0.3130	6.2
3. 0.420	4.2	0.2895	5.7
4. 0.458	4.5	0.3430	6.8

In assaying the drug, 10 grms. in a No. 60 powder are placed in an Erlenmeyer flask, and 25 cc. of alcohol are added. The flask is then fitted with a stopper through which is inserted a glass tube about 2 ft. long for a condenser, and left on a sand bath at 80° C. for three hours.

The contents of the flask are then transferred to a small percolator and washed with alcohol until about 50 cc. of percolate are obtained. When cooled to room temperature, the solution is made up to exactly 50 cc. Of this

solution 10 cc., representing 2 grms. of the drug, are used for assay, which is carried out in exactly the same way as described for the fluid extract, with the exception of the addition of the 5 cc. of alcohol, which is omitted.

It was found that it required at least 48 hours' maceration with cold alcohol to exhaust the drug, and hence the hot maceration is advisable.

Six different samples of podophyllum were assayed by this method, and from the same samples fluid extracts were made according to the directions in the United States Pharmacopœia, and were also assayed. The results are given below :—

	Grms. resin in 100 grms. drug.	Grms. resin in 100 cc. fluid extract.
1.	5.03	4.96
2.	5.24	5.16
3.	4.65	4.66
4.	4.92	4.89
5.	4.73	4.83
6.	6.82	6.71

These results show that the method gives very concordant results on the assay of the drug and fluid extract, and much higher results than the precipitation method. If the method gives equally good results in the hands of other workers, then it would be advisable that fluid extract of podophyllum, U.S.P., be assayed and standardised. As good lots of podophyllum drug contain 5 per cent of resin, a standard of 5 per cent resin for the fluid extract is suggested.

The method can also be applied to the assay of solid and powdered extracts of podophyllum by dissolving weighed quantities of the extracts in sufficient alcohol to render the solutions of about the same strength as fluid extract.—*Chemical Engineer*, xx., No. 3.

THE DETERMINATION OF CHROMIUM AND MANGANESE IN IRON AND STEEL.

By FRED C. T. DANIELS.

In steel-furnace operations it is frequently necessary to include chromium among elements to be determined in the preliminary analysis. The following twenty-minute method has been worked out to fill this necessity. It has been in constant use for the past two years and is sufficiently accurate to be used as a daily routine method, and it occupies but little of the chemist's actual working time.

The method for chromium is an adaptation of the persulphate method for the manganese determination in iron and steel.

The method for manganese is the persulphate method except that the sum of the manganese and chromium is obtained in this titration and the manganese calculated by difference, using the results from the chromium determination. The objection to the usual persulphate method for manganese, in the presence of chromium, is that a varying quantity of the chromium is reduced along with the manganese by the ferrous ammonium sulphate or sodium arsenite. If determined colorimetrically, the chromium gives the solution a different shade, which is difficult to compare. This may be overcome by using for a standard a steel containing approximately the same amount of chromium as the sample. A still more convenient way is to add the chromium as potassium bichromate, using a standard solution, so that 1 cc. would equal 0.0005 gm. of chromium, i.e., 0.25 per cent chromium for a 0.20 gm. charge of the sample. This solution is added to the standard after the solutions have been transferred to the colour comparison tubes.

Chromium.—Weigh 1 gm. of the sample into a 300 cc. Erlenmeyer flask (Jena glass), add 100 cc. nitric acid (1.135 specific gravity), place on the hot plate, and when

solution is complete, boil off all nitrous fumes. (The volume of the solution should not be less than 75 cc. It is unnecessary to filter off the silicon and graphite residue if the solution is complete. When the sample is high in combined carbon, it is well to add a few crystals of ammonium persulphate when the solution is complete and boil a moment longer to destroy the combined carbon). Remove the flask from the hot plate, add 75 cc. silver nitrate solution (2.00 grms. per litre), and immediately 5 grms. of ammonium persulphate crystals. Replace flask on the hot plate and bring gently to boiling. Boil vigorously for a minute, and while still boiling add dilute hydrochloric acid, drop by drop, until the permanganate colour is completely destroyed. Continue the boiling for one minute and then cool the flask immediately in water. Titrate by adding an excess of tenth-normal ferrous ammonium sulphate solution above that required to reduce the chromium, and titrate back with tenth-normal potassium permanganate solution. The number of cc. of the ferrous ammonium sulphate oxidised by the chromate, multiplied by 0.00174, gives the weight of chromium in the sample.

Manganese in the presence of Chromium.—Proceed according to the above directions for the determination of chromium except that after the ammonium persulphate is added, only heat until the solution just comes to boiling, then cool immediately and titrate as before, this time adding enough ferrous ammonium sulphate to reduce both the manganese and chromium. The number of cc. of ferrous ammonium sulphate used, minus the number used in the chromium determination, multiplied by 0.0055, equals the weight of manganese in the sample.

The ultimate value of the solutions may be used in calculations as above. In this case it is advisable to carry along a blank with a sample containing no chromium and subtracting the blank. The standardisation of the solutions against a standard steel is the most satisfactory procedure.—*Journal of Industrial and Engineering Chemistry*, vi., No. 8.

NOTICES OF BOOKS.

Complex Ions in Aqueous Solutions. By ARTHUR JAKES, D.Sc., F.I.C. London, New York, Bombay, Calcutta, Madras: Longmans, Green, and Co. 1914.

THE experimental methods which have been employed in the study of the formation of complex ions in aqueous solutions are described in this book, and illustrative examples are discussed to explain the principles involved. The author assumes only a very limited knowledge on the part of his readers, and the book is quite suitable for the use of students who are acquainted with the elements of physical chemistry. It will be found not very easy to read, and in some cases the explanations appear to be somewhat too much compressed, but the reader should be able by careful study to get from it a clear grasp of the experimental work done on ionisation.

The Rose of the Winds. By SILVANUS P. THOMPSON, D.Sc., F.R.S. London: Oxford University Press.

THIS paper on the origin and development of the compass card was read at the International Historical Congress in April, 1913. The author treated his subject under three headings:—The origin of the names of the winds, the origin of the arrangement of the Rose of thirty-two points, and the origin and significance of the distinctive marks used on compass cards, and gave much curious and interesting information relating to the evolution of the details of the compass card, and the different types which were in existence before 1650, since which date the cards of all European nations have shown hardly any variation.

Prospectus of University Courses in the Municipal School of Technology, Manchester, Session 1914-1915.

THE prospectus of the University Courses at the Manchester School of Technology contains syllabuses of the lectures and classes, and full information as to fees, &c. From the descriptions of the laboratories they appear to be excellently equipped, and the department of applied chemistry is reported to be particularly flourishing. Excellent opportunities are provided for advanced study and research, and the lecture courses are carefully planned. It is highly satisfactory to read that a considerable proportion of the best students, after taking their degree, devote one or two more years to research work in chemical technology.

Report on Radiation and the Quantum Theory. By J. H. JEANS, M.A., F.R.S. London: The Electrician Printing and Publishing Co., Ltd. 1914.

THIS report will be invaluable for students and others who wish to obtain a clear view of the bearing of the quantum theory upon physical science. Prof. Jeans, than whom no one is better fitted to perform the task, has explained and summarised modern work in a most lucid manner, and has produced an account which can be read equally profitably by those to whom abstract reasoning makes a greater appeal and those who, on the other hand, feel more interest in physical ideas. Thus the mathematics of the subject are practically relegated to two chapters, which may be omitted if desired. The references to the literature of the subject and to the discussion on radiation at the British Association Meeting in 1913 are comprehensive, and the bearing of the quantum theory upon the problem of the line spectra of the elements and the photo-electric effect is very clearly treated.

The Paper Makers' Directory of all Nations, 1914. London: Dean and Son, Ltd.

THE Paper Maker's Directory contains lists of British mills, and also of paper, pulp, and board mills in the Colonies and foreign countries. The mills are classified according to the principal goods produced, and the whole is arranged alphabetically to facilitate reference.

Williams' Fire-damp Indicator or Methanometer. Verbatim Report of Proceedings. 62-67, Norfolk House, Norfolk Street, Strand, London.

THIS is a verbatim report of the proceedings at a public meeting held in June, when Mr. Alfred Williams gave a demonstration of the apparatus he has invented for the detection and estimation of fire-damp in the atmosphere of mines. The apparatus and the ingenuity of the application of the principle upon which it is based—the detection of the rise of temperature due to the catalytic action of platinum black towards mixtures of air and inflammable gases—were first described in enthusiastic terms by Prof. Silvanus Thompson, F.R.S.; and Dr. J. Erskine-Murray presented his report upon the working of the instrument. The apparatus is portable and simple, and by means of it very small percentages of methane (probably less than half per cent) can be detected. The delegates from the Miners' Federation of Great Britain, who were present at the meeting, expressed their high opinion of the value of the methanometer.

Decomposition of Calcium Carbide.—E. Briner and A. Kuhne.—When calcium carbide is heated it simply undergoes decomposition into its elements, no subcarbide being formed. The decomposition resembles that of all exothermic compounds, and becomes more complete and more rapid as the temperature rises. The reaction is reversible. The decomposition is accelerated when the carbide is powdered and heated *in vacuo*.—*Journal de Chimie Physique*, 1914, xii., [3], 433.

CORRESPONDENCE.

CAPTURING GERMAN TRADE.

BET SUGAR: BRITAIN'S UNPARALLELED OPPORTUNITY.

To the Editor of the Chemical News.

SIR,—At a time when the eyes of the British manufacturer are eagerly turned towards the possibility of the capture of at least a large proportion of Germany's trade, which to an extent may now be said to be going a-begging, it is permissible to turn to an aspect of the situation which holds boundless opportunities for the British agriculturist chiefly, but is also a matter of very great moment to manufacturers and workers as well. I refer to an industry which has been very frequently mentioned in the Press of the country and which now appears to provide a solution for many of the difficulties which confront the British agriculturist, whether as a farmer engaged in the cultivation of his own or another's land, or as a landed proprietor whose farming land has deteriorated in value, where it has not actually gone out of cultivation. Some very remarkable, and in the main successful, experiments have been of late years made by the farmers and landowners in the production of beet for sugar producing purposes, and the results already achieved in the face of difficulties, which must confront every new departure, are in the highest degree encouraging.

These experiments have given every promise of ultimate, and it might be said enormous success, even under the conditions which prevailed previous to the present war, when the growers of beet in England had to face the keen competition of an already established industry on the Continent, chiefly in Germany and Austria; but now that this competition has been effectually "closed down" as the result of the great European war, there is every reason to look for a huge success which should put the English industry on its feet, if the present advantageous situation be utilised to the extent which is demanded not only by the opportunity offered but also by the absolute needs of this country. How great these needs are will be indicated by the following figures, which show what are the demands made by sugar consumers of this country upon our Continental neighbours. During 1912, the last year available for an actual statement of the industry, the quantity of beet sugar imported into the British Isles from six Continental centres has been as under:—

Refined Sugar.

Country.	Tons.	Average price per ton f.o.b., foreign port.	Total.
Germany	453,500	£12	—
Austria	175,700	£12	—
Holland	189,400	£12	—
Belgium	64,900	£12	—
France	35,200	£12	—
Russia	9,200	£12	—

927,900 at £12 = £11,134,800

Raw Sugar.

Country.	Tons.	Average price for 1913 f.o.b., foreign ports.	Total.
		£ s. d.	£
Germany	440,600	9 10 0	—
Austria	148,500	9 10 0	—
Holland	28,400	9 10 0	—
Belgium	27,700	9 10 0	—
Denmark	35,500	9 10 0	—
France	634	9 10 0	—
Total—			

Raw sugar .. 681,334 at 9 10 0 = 6,472,673

Refined sugar .. 927,900 „ 12 0 0 = 11,134,800

Tons 1,609,234 = 17,607,473

From these figures it will be easily seen what a preponderating share of the trade was held by Germany and Austria, in fact their share of the total of £17,607,000 was £13,149,000. Now the bulk of this business can be secured by the British farmer and manufacturer, for, apart from the fact that Germany and Austria as competitors will be crippled for years to come as a result of the war, the sugar supply of the British Isles must be had from somewhere, and who is in a better position to step into the breach than the British farmer. One result of the experiments in the growing of beet in these islands, is to prove that not only is our soil well suited for beet production, but the yield per acre is equal in most cases to that of Continental centres, and in many instances much better. This, coupled with the fact that the land is enriched by beet cultivation, so that other crops grown in rotation yield very much better results, should prove an incentive to the farmer and increase the area he has under beet, or if he has none, to make an early start.

This is sufficiently borne out by the results obtained where the experiment has been tried, and the larger the scale the greater the satisfaction with the result. In a report issued by the Board of Agriculture and Fisheries, on "Experiments in the Cultivation of Sugar Beet in 1912," the Board says:—

"There is no question that beet with a high sugar content can be grown in this country and give yields equalling, if not exceeding, those obtained on the Continent, and the information given in this report shows that farmers who wish to form their own opinion on the comparative merits of beet and other root crops may, without difficulty and at little cost, grow the crops for themselves."

Reports both from Germany and the United States show the wheat yield on land previously used for beet increased by 77 per cent, and rye as much as 96 per cent, while at Hayle in England, similar results have been obtained, although the increase has not been quite so great as the figures given above indicate in the case of Germany. It is sufficiently great, however, to demand the serious consideration of those who are living on the land. Of late years a very considerable portion of the farming land of the country has gone out of cultivation from various causes, and if a serious effort were made to put this land and much more under beet, the result would not only be profitable to the growers, but would mean the establishment of an industry in the Kingdom which would have a very material effect in checking the growing tendency to unemployment which is so marked a feature of industry during the present time. Factories to deal with the beet would require to be provided. An important feature of the sugar beet industry is that a number of exceedingly valuable by-products are associated with the production of beet sugar. The pulp finds a very ready market, for it is often less than the demand for it, while the leaves are an excellent cattle food, and the saturation lime is a splendid fertiliser.

The experience of the United States should provide a valuable object lesson to this country. The number of acres of beet under cultivation has trebled in ten years despite the fact that in the same period the yield per acre has nearly doubled, while the price per ton of beet has gone up nearly 40 per cent. Last year the total quantity of beets grown yielded 5,834,000 tons (of 2000 lbs. each) a figure which exceeds by 34 per cent the average of the five previous years. The value was £6,800,000 at the factory, which is 48 per cent higher than the preceding five years average. One feature of beet sugar cultivation which ought specially to attract the farmer is that it grows his roots on the contract basis. He agrees with the factory to plant a certain acreage in beet for a given number of years. He sows his seed in April and draws payment in November, and during the delivery of the roots payments are made on account if desired. Experience has shown that a dividend of from 10 to 15 per cent may be looked for with every confidence. On the Continent dividends have ranged from 10 to 53 per cent.

The value of such an industry as that of the production of beet sugar has been quickly recognised by responsible public men, both within and without the Government. Mr. Bonar Law is equally emphatic with Mr. Balfour that the growing of beets would prove a valuable help to the agriculture of the country, and Mr. Bonar Law adds that if our business had been conducted as a business man would conduct his own affairs, the sugar beet industry would have been introduced into this country long ago. It is even more interesting to note the encouragement given by Mr. Asquith when he stated in the House of Commons, "That no objection could be seen by the Government to help being given to the industry in its early days from the Development Fund." This is a sufficiently plain indication that the Government are wisely prepared to do their share of the pioneer work—a work which has already shown every prospect of abundant success.

The association of which I have the honour to be chairman has, for nearly five years, carried on a vigorous educational work throughout the country, and those who are interested in the subject may obtain copies of pamphlets and reports issued by the association upon application to the Secretaries, 24, North John Street, Liverpool.—I am, &c.,

E. RUSSELL TAYLOR,
Chairman of the Council of the Incorporated
English Beet Sugar Pioneer Association.

41, Castle Street, Liverpool,
October 14, 1914.

PHOSPHORUS AND CARBON.

To the Editor of the Chemical News.

SIR,—I should like to call attention to the fact that carbon and phosphorus resemble each other in certain respects, especially since this connection was implied by the tabular scheme shown in the CHEMICAL NEWS, cix., 133.

Prof. H. C. Jones ("A New Era in Chemistry," 1913, p. 183) says:—"Phosphorus exists in at least four forms; ordinary red phosphorus, ordinary white phosphorus, really white phosphorus, and black phosphorus. Carbon exists in a great many forms. We have the diamond, graphite, and Moissan has found a large variety of forms of amorphous carbon."

Newth's "Inorganic Chemistry," p. 456 and p. 459, says:—"Phosphorus is volatile at ordinary temperatures; if a small quantity of phosphorus be sealed in a vacuum tube, and the tube be placed in the dark, the phosphorus will slowly vaporise; and if one end of the tube be kept slightly cooler than the rest, the phosphorus will sublime upon that part in the form of brilliant, colourless, and highly refracting rhombic crystals, which retain their beauty as long as they are kept in the dark. The density of the vapour of phosphorus is 62.0, giving a molecular weight of 124.0, which is four times the atomic weight, showing that the molecule of phosphorus contains four atoms. Even at temperatures as high as 1040° these tetra-atomic molecules are stable, but it has been shown that at high temperatures dissociation begins to take place . . . Red phosphorus may be obtained in the form of rhombohedral crystals by heating the substance under pressure to a temperature of 580°."

P. W. Bridgman (*Journ. Am. Chem. Soc.*, 1914, xxxvi., 1344) has discovered two new modifications of phosphorus which he summarises in his paper as follows:—"The first is a new modification of ordinary white phosphorus, possibly hexagonal with reversible transition point at atmospheric pressure at about -76.9°. The second modification, black phosphorus, is obtained irreversibly from white phosphorus at 12,000 kg./cm², and 200°. A number of its physical constants have been determined. Particularly striking are its high density, 2.691, and fair electrical conductivity."

"No attempt to transform either white or red to black

phosphorus has been successful by any other method except that above. Finally, some conjectural explanations of the relations of the various modifications have been given."

In a previous paper, Bridgman (*Phys. Review*, Feb. and March, 1914) describes the black variety of phosphorus as greyish-black, like graphite, which breaks with a similar greasy-looking fracture, and will mark on paper.

It will be seen that carbon and phosphorus have some peculiarities more or less in common. Doubtless relationship can be traced in other ways. For example, hydrogen phosphide (P₂H₄) calls to mind acetylene (C₂H₂), or rather ethylene (C₂H₄), which has a somewhat pleasant ethereal smell, the resemblance suggesting a sort of bromine-chlorine parallel.—I am, &c.,

F. H. LORING.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clix., No. 6, August 10, 1914.

This number contains no chemical matter.

No. 7, August 17, 1914.

Action of Radium Emanation upon Detonating Gas.—Otto Scheuer.—When detonating gas is exposed to the action of α -rays a very violent reaction occurs. In one case the flask was shattered by an explosion. The ratio $\frac{b}{a}$ is constant, as in the case of the decomposition of water (a =number of pairs of ions formed per curie-second, b =number of molecules of gas re-combined per curie-second). The analyses of the gas showed that the H₂O and H₂O₂ are formed. The water is probably formed chiefly by the decomposition of the peroxide. No ozone is formed.

Optical Activity of Compounds without Carbon.—A. Werner.—By the investigation of dodecaminehexol-tetracobaltic salts the author has shown that rotatory power is a property that belongs to compounds not containing carbon. The active bromide is brownish grey in colour and very soluble in water. In solution the rotatory power diminishes very rapidly, and the solution is inactive after two hours.

MISCELLANEOUS.

Battersea Polytechnic.—The following course of eight advanced lectures has been arranged:—"Structure of Crystals," by T. Martin Lowry, D.Sc., F.R.S., on Fridays, October 23, 30, November 6, 13, 20, 27, December 4 and 11, 1914, at 7 p.m. *Syllabus*.—The fundamental properties of crystals; real and ideal crystals; the external form of crystals; crystal symmetry; symmetry of the cube and octahedron; the cubic system; fundamental and derived forms; systems of lower symmetry; hemihedrism and hemimorphism; optical activity and pyroelectricity. The physical properties of crystals; liquid crystals; the crystallisation of metals; influence of hard-working and annealing on the properties and structure of metals. Isomorphism and polymorphism; vicarious replacement in minerals; isopolymorphism. The internal structure of crystals; space lattices; topic axial ratios; theories of Barlow and Pope; valency volumes and equivalence parameters. Application of Röntgen rays to the determination of crystal structure; work of Laue and Bragg.

THE CHEMICAL NEWS.

VOL. CX., No. 2866.

NOTES ON PLANT CHEMISTRY.

By P. Q. KEEGAN, LL.D.

Some Little-known Plants.

SOME results of my own researches among certain disregarded plants, seldom noticed or analysed, may be presented. There is a rare but conspicuous inhabitant of wet and boggy areas hereabouts, which is known as the grass of Parnassus (*Parnassia palustris*). The whole plant was extracted by boiling water, and the solution filtered, &c. It was found to contain a moderate amount of mucilage and no nitrate. It yielded reactions of a tannoid which seemed to be rutin, and also of a catechol tannin (some 2 or 3 per cent), which reacted as usual with HCl-vanillin, fir-wood, diazonium chloride, and formaldehyde; boiled with HCl a fine red colour and precipitate appeared, which were both greened by ammonia, its copper salt was soluble in ammonia, and with Millon's reagent it gave a red and greenish solution and a red-brown precipitate. This species is sometimes placed in the order Saxifragaceæ or near the Polygalaceæ, but according to the chemical analysis it is more like a St. John's wort (*Hypericum*). In any case, considering its dimensions, &c., it is decidedly tanniferous.

Another plant that grows in bogs is the butterwort (*Pinguicula vulgaris*), and is placed in the same alliance as the foxglove, speedwell, &c. It contained a good deal of mucilage, cane-sugar, and tannoid, but no tannin. The purified extract yielded specially fine orange colorations or precipitates with baryta-water, and with tin, lead, aluminium salts. The solution boiled with HCl gave a smutty crystalline precipitate, and this extracted by ether and evaporated gave a splendid orange solution with sulphuric acid; it gave no paracarthamin, and on potass fusion only a little phloroglucol. It was rather difficult to decide what this tannoid was; it seemed to resemble quercitagenin associated apparently with a catechin-like substance. There was no nitrate.

A bright yellow flowered plant, which seems to enjoy the cool drip of a mountain rill, especially in a snug shady position, is the golden saxifrage (*Chrysosplenium*). The analysis of a small clump got at the end of April showed that it produces much mucilage with some gum, a little nitrate, some cane-sugar, and a little tannin, but no tannoid. The tannin was a true catechol, one without any pyrogallol derivative. There was also a substance present with a quinol group (1:4). There are curious tannin vesicles scattered among the epidermal cells of this plant, like as in grass of Parnassus, but the latter is of much slower growth and has mycorrhiza on its roots.

That well-known and useful shrub known as mahonia or holly-leaved barberry, has been examined with reference to the existence in its bark of the alkaloid named berberine, but no one as yet has noticed the remarkable chemical resemblance of its leaves to those of the common ivy. Both contain caffetannin, and also a tannoid probably identical with quercitagenin. Here are some reactions common to the aqueous extracts of both leaves:—With very dilute potass a yellow passing to deep green and brown colorations reddened by acid, with lime-water or baryta-water the same effect; a few drops bicarbonate of sodium were added to some of the extract in a test-tube, there was no change at first, but presently a fine green appeared at the top of the liquid, which in the course of a few hours reached to the bottom, and on now adding acid in excess a red colour appeared; both solutions showed about the same reducing power as regards bichromate of potass,

oxide of silver, &c., and both contained much limy mucilage, some nitrate, and a good deal of cane-sugar. But while mahonia leaf contained more caffetannin, that of ivy was considerably richer in tannoid. The green reactions just described are decidedly rare in the chemistry of plants; something similar occurs in the extracts of the barks of holly, ash, snowberry, magnolia, &c., but these pale into insignificance in comparison, and, moreover, in these latter the effect very probably depends not on a tannoid, but on the intermixture of a very small quantity of an oxidation product (viridic acid) of the caffetannin itself, just in the same manner as the catechol tannin of oak, chestnut, black currant, &c., is found associated with a little gallotannin or gallic acid, also an oxidation product thereof. Other greens—which, however, are probably yellowed blues—appear in extracts such as that of bayberry bark or the leaves of bearberry, pæony, &c., and depend on the presence of a pyrogallol tannoid named myricitrin; these greens, however, tend to become blue, whereas the caffetannin greens tend to become brown owing to the formation of benzoquinone. Mahonia produces blue berries, which, as seen on a long clump facing the shore of Windermere Lake on a bright September morning, present a remarkable spectacle. True blue berries are extremely rare, but certain species of ash, *Lonicera*, and *viburnum* also exhibit them, and in all these cases the presence of caffetannin as chromogen supplies an explanation.

That grotesquely flowered plant, an emigrant from Western America, and known as the monkey flower (*Mimulus luteus*), which has diffused here most aggressively along rill sides and damp woods, has never yet, I think, been analysed. Accordingly I undertook the task, and found that it contained nitrate and about 1 per cent of caffetannin; the extract boiled with dilute sulphuric acid and shaken with ether, a substance was got which with acetic and HCl gave a green coloration and precipitate; there was a bitter principle soluble in benzene and in sulphuric acid with purplish colour; there was no rhinanthin or tannoid. According to these results this plant is, as it has been, properly placed in the Antirhoideæ section of the Scrophulariaceæ, near foxglove, gratiola, &c., and not associated with such plants as red and yellow rattle, bartsia, eye-bright, cow-wheat, all of which contain rhinanthin, are generally parasites, and produce only feeble quantities of nitrate or of tannin.

With regard to the chemical differences which the roots and leaves of the same plant display, the case of the wild geranium (*G. sylvaticum*) may be instanced. The root parts (rhizome) of this plant on July 26 contain no nitrate or saccharose, but a considerable quantity of starch and oxalate of calcium, and a catechol tannin with a little gallotannin; the solution precipitated tartar-emetic at once, and on soda-fusion gave protocatechuic acid as the chief product. The leaves, on the other hand, contained a little nitrate, much saccharose, with considerable gallotannin and tannoid, and very little catechol tannin; the solution gave with Millon's reagent a splendid pure blue coloration, passing to green and red, and potass fused gave phloroglucol and pyrogallol. These differences are not to be explained by the anatomical structures of the organs concerned, as in the case of barks, but by the fact that in rapidly growing plants the soluble nitrogen of the leaves flows to the flowers and fruits, while at the same time the soluble sugars decrease in the stem and roots. The overflow from leaf to flower would induce a more intense de-assimilation in the former organ, with production of a more highly oxidised tannin, as again the overflow from petal to ovary would induce the production of a pseudo-blue pigment in the corolla.

Many lilies and plants of the order Liliaceæ have been examined with respect to their medicinal and other qualities, but to the ordinary plant analyst they are pretty much of a sealed book. In the course of a search for chromogenic principles, I noticed a peculiar red tint on the stem of what is known as the turk's cap or martagon lily,

and I proceeded to analyse the leaves of that plant. I found no nitrate or saponin therein, but there was evidently a good deal of tannoid. Seeing that the lead salt of the extract dried up green, and on extracting it with alcohol and dilute sulphuric acid, boiling the solution, and adding a little FeCl_3 and a very slight excess of carbonate of soda, a red-violet coloration was decidedly produced, I applied other tests for caffetannin. The result was, although rather a close shave, that I convinced myself that caffetannin was actually produced by this monocotyledon. An examination of the leaves of the day-lily (*Hemerocallis flava*) yielded a similar result, and these discoveries, in view of the ignorance or indifference prevailing on this subject, seem well worth recording here, especially in connection with the chemistry of the floral pigments (CHEM. NEWS, 1913, cvii., 181).

Recent Plant Physiology.

One of the most important views or theories respecting vegetable physiology of late proposed is that published by Pantanelli and Faure, according to which the assimilatory (synthetic) processes in the leaf take place while the protoplasm is alkaline, whereas the deassimilatory (analytic) processes increase in intensity when the protoplasm, gradually yielding to the acid reacting sap, becomes acid. Only a brief allusion to this subject can be undertaken here. Vegetable liquids tend generally to be acid, and the youngest parts of plants are the most acid, *i.e.*, their sap contains most free acid or soluble acid salts. There is no doubt, however, that these statements refer only to the total sap extracted or expressed from the whole organ. It is extremely probable, on the other hand, that the various tissues of any single organ may react differently in this respect; for instance, the palisade tissue of a leaf may be alkaline or neutral, while the upper epidermis and the conducting cells of the vascular bundles may be acid. The medullary rays of the wood are certainly not acid, while most of the bast and cortex may be strongly acid. In some cases the quantity of recognisable acid may be very small, as in Scot's pine, spruce, several grasses, crucifers, beans, and composites, but any of these may have intense de-assimilation. There is no starch in the ripe seed of white lupine, while that of haricot may have abundant starch; the former has much oxalate, the latter much less. A lengthy series of illustrations of this kind could be adduced, but a striking fact revealed by the analysis of forest leaves at different stages of growth may be here considered. In the young leaf tannoids alone are frequently produced, only later on do tannins appear; the former therefore seem to be the product of an alkaline protoplasm, the latter of an acid protoplasm. With the tannoids are associated volatile oils, resins, and waxes; with the tannins the organic acids, especially oxalic, are mated. In the autumn fallen leaves of the plane tree of the London squares I found still much tannoid and only a little tannin, while the ash of the leaves yielded only 22.5 per cent CaO . On September 30 a little tannoid but more tannin was found in Sycamore leaves, the ash of which yielded 31.5 per cent CaO (41.9 in autumn fallen leaf). Formerly it was stated that all tannins were acids; at the present time the only tannin recognised as such is caffetannin. Many other plant constituents were called acids when first discovered; for instance, æsculin, atranorin, chlorogenin, quercitrin, rutin, maclurin, &c., but these seem to combine with metallic inorganic salts as "lakes" only, and do not yield CO_2 when heated alone or with lime. That "bases engender acids" is a chemical principle, but in the case of the formation of tannins there is no question as to the influence or participation of bases, either organic or inorganic. According to Schwarz the alkaline reaction (as shown by Pfeffer) of the protoplasm in the higher plants probably does not depend on the presence of ammonia or ammonium compounds; it is dependent on its basicity. When, however, by the exhaustion of its chemical activity, *i.e.*, by the cessation of its assimilatory function, it loses its power of what may be called sustentation, it, like many

other organic products, becomes acid, and in this condition it is best fitted to deassimilate. While deassimilation can never be nil in a living cell, whereas assimilation therein may be annulled completely, it is obvious that the former may act under either alkaline or acid conditions of the sappy medium. The special constituent of the tannoids is the invariable presence of an unsaturated reactive and reductive group CO , which seems to exist in a free condition; their structure is compact, *i.e.*, the atomic groups of the compounds into which they may be broken by oxidation or reduction are never free enough to allow of their existence being revealed or suspected beforehand. The reverse is the case with the tannins; we can tell with absolutely accuracy by a certain treatment of the tannin itself whether it contains a phloroglucol or a pyrogallol group, or whether it contains neither one nor the other group; the inference is that certain of their atomic groups are free, and that the total molecule is more of a "lake" perhaps than a true compound. Whether this peculiar structure is due to their being formed in an acid medium is a question that would require some investigation. The fact that tannoids are very rarely, if ever, produced in barks or roots may be taken as a significant basis on which to build this inquiry.

Patterdale, Westmoreland.

THE PREPARATION AND PROPERTIES OF THE NEUTRAL AMMONIUM SALTS OF ORGANIC ACIDS.

By LE ROY McMASTER.

As stated in two previous papers, most of the ammonium salts of organic acids described in the literature are the acid salts instead of the neutral salts (Keiser and McMaster, *Am. Chem. Journ.*, 1913, xlix., 84; CHEM. NEWS, 1913, cviii., 136; McMaster, *Am. Chem. Journ.*, 1913, xlix., 294; CHEM. NEWS, 1913, cviii., 182). Many of the "neutral" salts purchased have also been found to be "acid." This is due to the fact that they have been prepared by neutralising the aqueous solution of the organic acid with ammonia water or ammonium carbonate, and the solution allowed to evaporate to crystallisation. The salts thus formed are generally hydrolysed, and the acid salt results. Many of these salts also contain water of crystallisation. Neutral ammonium salts free from water of crystallisation can be obtained by passing dry ammonia gas into an absolute alcohol or ether solution of the organic acids. Most of the organic ammonium salts are insoluble in alcohol or ether, and are thus precipitated. Keiser and McMaster prepared by this method the neutral ammonium salts of fumaric, maleic, mesaconic, and citraconic acids. I prepared, also, by this method the neutral ammonium salts of propionic, isobutyric, benzoic, cinnamic, malonic, succinic, malic, tartaric, *o*-phthalic, and *m*-phthalic acids, and studied some of their properties. Many of the properties of the salts made by this method were found to be different from those as described in the literature. This has also been found to be the case with some of the ammonium salts of the organic acids described in this paper.

The work on the preparation and study of the properties of the neutral ammonium salts of organic acids has been continued. They were prepared in both absolute ethyl alcohol and ether. Several were prepared also in methyl alcohol. In several cases the salts were more or less soluble in the alcohols, and, under this condition, they were prepared only in ether. When the experiments were carried out in ethyl alcohol it was generally necessary to keep the flasks surrounded by cold water, for, when the ammonia was passed into the solution, heat was set free, due to the action of ammonia on the alcohol and also to the heat of neutralisation. Very little, if any, heat was developed when ether was used as the solvent for the acid.

Whenever the ammonium salts are only slightly soluble in ethyl alcohol, they were prepared in this medium rather than in ether, since from an alcoholic solution of the acid they are generally precipitated in a crystalline form. From an ethereal solution they are mostly precipitated in an amorphous state. The neutral ammonium salts were all filtered and washed by suction on alundum crucibles. The organic acids used in this investigation were obtained from Kahlbaum or Schuchardt.

Ammonium Butyrate.—No record can be found of the preparation of this salt other than being mentioned by Pelouze and Gélis as being a deliquescent compound (*Ann.*, lxxvii., 249). When dry ammonia gas was run into an ethereal solution of normal butyric acid, a white, granular, crystalline precipitate of neutral ammonium butyrate was formed. The precipitate was quickly filtered by suction on an alundum crucible, washed with ether, and then placed in a vacuum desiccator for a few minutes. The salt is deliquescent, and loses ammonia readily on standing in the air. On first dissolving the salt in water the solution is neutral. The solution soon turns acid, due to hydrolysis. The salt is readily soluble in methyl alcohol, ethyl alcohol, and acetic acid, and appreciably so in acetone.

Calculated for $C_4H_7O_2NH_4$, 13.33 per cent; found, 13.31 per cent N.

Ammonium Isovalerianate.—Beilstein states that an acid salt of isovalerianic acid of the formula $NH_4C_5H_9O_2 + 2C_5H_9O_2$ is used in medicine. The U.S. Dispensary describes the commercial valerianic acid as a mixture of two isomeric acids—isovaleric acid and optically active valeric acid. This is true of the valeric acid that is obtained from the *Valeriana officinalis*, the *Angelica archangelica*, and that which results from the oxidation of the amyl alcohol of fermentation with the aid of chromic acid. The "ammonium valerianate" described in the Dispensary is evidently a mixture of ammonium valerianate and ammonium isovalerianate. It is also acid. Hager ("U.S. Dispensary," 18th edition, p. 463; *Pharm. Centralb.*, 1879, p. 465) states that commercial ammonium valerianate is always the acid salt, as is proved by the acid reaction and the strong rotation of the crystals when placed upon cold water; the neutral salt is obtained only with difficulty, is in prismatic crystals, and is easily liquefied by moderate temperatures. A sample of ammonium valerianate purchased from Kahlbaum was found to be acid. The neutral ammonium salt of isovalerianic acid was prepared by conducting dry ammonia gas into an ethereal solution of the acid. There was formed a snow-white crystalline precipitate which is very deliquescent, and which has an odour like that of the free acid. The salt is very soluble in water. On first dissolving the salt in water the solution is neutral, but soon becomes acid, due to hydrolysis. It is readily soluble in methyl alcohol, ethyl alcohol, acetic acid, and somewhat so in acetone.

Calculated for $C_5H_9O_2NH_4$, 11.76 per cent; found, 11.77 per cent N.

Ammonium Caproate.—No record can be found of the preparation of this salt. Caproic acid was dissolved in ether, and ammonia passed into the solution. A white precipitate formed, which at first was somewhat gelatinous, but soon became crystalline and translucent. The salt is very deliquescent, and has to be filtered and washed very quickly by suction. When dissolved in water a neutral solution is formed, which soon becomes acid. The salt is very soluble in methyl alcohol, ethyl alcohol, and acetic acid. On standing in the air it readily loses ammonia. Analysis proved it to be the neutral ammonium caproate.

Calculated for $C_6H_{11}O_2NH_4$, 10.52 per cent; found, 10.53 per cent N.

Ammonium Crotonate.—On passing ammonia gas into a saturated alcoholic solution of crotonic acid a beautiful

glistening white precipitate formed. The precipitate was quickly filtered, washed with ether, and dried for a short time in a vacuum desiccator. The ammonium salt was also prepared in ether. When ammonia gas was passed into an ethereal solution of the acid, there was first formed a very gelatinous precipitate, which soon became an amorphous powder. The salt prepared in either medium is not hygroscopic, but is very soluble in water. The aqueous solution is neutral, but soon hydrolyses. The neutral ammonium salt, both crystalline and amorphous, has the odour characteristic of crotonic acid. It is readily soluble in methyl alcohol, ethyl alcohol, and acetic acid, but insoluble in ether and chloroform.

Prepared in alcohol—Calculated for $C_4H_5O_2NH_4$, 13.60 per cent; found, 13.61 per cent N.

Prepared in ether—Found, 13.60 per cent N.

Although many of the salts of crotonic acid have been prepared and studied, no mention of the neutral ammonium salt can be found.

The Ammonium Salt of Ethyl Malonic Acid.—When ammonia gas was run into an alcoholic or an ethereal solution of ethyl malonic acid, there was first formed a white precipitate which is somewhat mucilaginous. This precipitate after a short time changed to a semi-crystalline one when prepared in alcohol, and to an amorphous powder when prepared in ether. The salt prepared by either method is somewhat hygroscopic, and loses ammonia readily in moist air. The salt was filtered by suction, washed with ether, and dried in a desiccator. When dry the salt has the appearance of dry paper pulp. The aqueous solution was neutral to sensitive litmus paper. It is slightly soluble in ethyl alcohol, readily soluble in methyl alcohol and acetic acid, but insoluble in acetone. A solution of the salt is not precipitated by ferric chloride. No mention of this salt is made in the literature.

Prepared in alcohol—Calculated for $C_5H_6O_4(NH_4)_2$, 16.86 per cent; found, 16.87 per cent N.

Prepared in ether—Found, 16.87 per cent N.

Ammonium Glutarate.—When ammonia is passed into an alcoholic solution of glutaric acid there is formed a white amorphous precipitate, which soon becomes crystalline and granular in appearance. This salt can also be prepared in ether. The salt thus formed is the neutral ammonium glutarate, soluble in water, methyl alcohol, and acetic acid. It is insoluble in ether. The salt is not deliquescent.

Calculated for $C_5H_6O_4(NH_4)_2$, 16.86 per cent; found, 16.85 per cent N.

Ammonium Adipate.—This salt has been prepared by Dieterle and Hell (*Ber.*, 1884, xvii., No. 2221) by treating an aqueous solution of adipic acid with an excess of ammonia water, and evaporating the mixture to crystallisation. Small, glittering leaflets were formed. Larger crystals of the neutral salt were obtained by allowing the aqueous solution to evaporate spontaneously in an atmosphere of ammonia. The salt is described as being stable in the air. It loses one molecule of ammonia when dried at 100°, forming the acid salt. Upon heating the salt to 120–150°, all of the ammonia is driven off and the free adipic acid is formed. This salt has also been described by Arppe as forming monoclinic crystals (*Zeit. Chem.*, 1865, p. 301).

Ammonia was passed into an alcoholic solution of adipic acid, and a white crystalline salt was formed. It was filtered, washed with alcohol and ether, and dried in a desiccator. The salt is stable in the air, and an aqueous solution of it is neutral. It is slightly soluble in ethyl alcohol and insoluble in ether. It is appreciably soluble in methyl alcohol, from which it crystallises in small, beautiful leaflets. Determination of the nitrogen proved it to have the composition of the neutral salt.

Calculated for $C_6H_8O_4(NH_4)_2$, 15.55 per cent; found, 15.50 per cent N.

Ammonium Pimelate.—This salt would not precipitate when ammonia gas was run into an alcoholic solution of pimelic acid, due to its solubility in alcohol. When ammonia gas was passed into an ethereal solution of the acid a white gummy precipitate was formed which would not crystallise. Ammonia was then passed into a solution of the acid dissolved in alcohol and ether. A fine white powder was formed which was filtered, washed with ether, and dried in a desiccator. This salt gave a neutral solution when dissolved in water, in which it is very soluble. It is not hygroscopic, but loses ammonia very readily in both dry and moist air, passing to the acid salt. It is quite soluble in methyl alcohol and acetic acid. It crystallises from ethyl alcohol in leaflets. Analysis showed it to be the neutral ammonium pimelate.

Calculated for $C_7H_{10}O_4(NH_4)_2$, 14.43 per cent; found, 14.40 per cent N.

Ammonium Sebate.—Neison (*Journ. Chem. Soc.*, xxvii., 301) states that the ammonium salts of sebacic acid can be obtained in solution, but they are invariably partially decomposed, with loss of ammonia, on attempting to obtain them in the solid state, whether the evaporation is conducted *in vacuo*, at the heat of a water-bath, over sulphuric acid, or spontaneously in a current of dry air.

The neutral ammonium salt of this acid was prepared in a solid state by the usual method in both alcohol and in ether. When precipitation takes place in alcohol, there is first formed a slightly gelatinous precipitate which changes to a white crystalline powder. When prepared in ether the white powder is not crystalline. The precipitate in each case was filtered, washed with ether, and dried for a short time over sulphuric acid in a vacuum desiccator. The salt is readily soluble in water, to which it imparts a neutral reaction. The salt was still neutral to litmus after standing for one month in a tightly stoppered bottle. It is not deliquescent, but loses ammonia in moist air. It is slightly soluble in ethyl alcohol. The salt crystallises from methyl alcohol in small crystalline flakes.

Analysis of the salt prepared in alcohol showed it to be the neutral ammonium salt of sebacic acid.

Calculated for $C_{10}H_{16}O_4(NH_4)_2$, 11.86 per cent; found, 11.86 per cent N.

Ammonium Tartronate.—Petriew describes this salt as needles which decompose at 100° (*Journ. Russ. Chem. Soc.*, x., 152). Tartronic acid was dried at 100° , at which temperature it loses its water of crystallisation, dissolved in alcohol, and ammonia conducted into the solution. A fine glistening white crystalline precipitate formed. This salt was filtered, washed with ether, and dried in a desiccator. It is not deliquescent, and an aqueous solution of it is neutral to different indicators. It is insoluble in methyl alcohol and ether. When treated with acetic acid, free tartronic acid is formed.

Calculated for $C_3H_2O_5(NH_4)_2$, 18.18 per cent; found, 18.17 per cent N.

Ammonium Racemate.—Racemic acid was dried at 100° , and ammonia passed into an alcoholic solution of it. A white precipitate, somewhat flocculent at first, was formed. This changed to a crystalline powder, which as soon as neutral, was filtered and washed with alcohol and ether. An aqueous solution of the salt was neutral towards different indicators. The salt is not deliquescent. It is insoluble in methyl alcohol, ethyl alcohol, and ether.

Calculated for $C_4H_4O_6(NH_4)_2$, 15.21 per cent; found, 15.21 per cent N.

Ammonium Itaconate.—Baup (*Ann.*, xix., 29) states that, like many other ammonium salts, neutral ammonium itaconate does not crystallise, since on evaporation or standing in the air it loses ammonia and the acid salt forms.

When ammonia gas is passed into an alcoholic solution of itaconic acid, until a portion of the salt on being dissolved in water shows a neutral solution, there is formed a

white granular crystalline precipitate of neutral ammonium itaconate. When the ammonia is first passed in, the precipitate formed is slightly gelatinous. The salt was washed with alcohol and ether, and dried for a short time over sulphuric acid in a vacuum desiccator. It is very hygroscopic. In dry air the salt is stable, but loses ammonia in moist air. It is soluble in acetic acid, but insoluble in methyl alcohol, ethyl alcohol, and acetone.

The neutral ammonium salt of itaconic acid can also be precipitated in ether as an amorphous compound. The salt prepared in either alcohol or ether readily hydrolyses when dissolved in water.

Prepared in alcohol Calculated for $C_5H_4O_4(NH_4)_2$, 17.07 per cent; found, 17.07 per cent N.

Prepared in ether—Found, 17.07 per cent N.

Action of Ammonia on some other Organic Acids.—Attempts to prepare the neutral ammonium salts of isosuccinic, pyrotartaric, aconitic, and several other acids have so far given unfavourable results. The precipitates formed were usually very mucilaginous and would not crystallise, even if the ammonia was conducted into the alcoholic or ethereal solution for a long time. Methyl alcohol was tried as a medium in which to precipitate these salts but without success. Work on these acids is being continued. A number of neutral ammonium salts of the higher fatty acids and of the aromatic series have been prepared and analysed. The results will be given in a future paper. This investigation is being continued with other organic salts.—*Journal of the American Chemical Society*, xxxvi., No. 4.

OIL-HARDENING PLANT IN NORWAY.

COMMERCIAL Agent Erwin W. Thompson reports that during the summer of 1913 an oil-hardening plant was opened at Fredrikstad by De Nordiske Fabriker, with head offices at Christiania. The original object was to harden whale oil for the soap industry, but as the result of experiments with edible oils the plant is being enlarged to a capacity of 1000 barrels a day, with the expectation of hardening cotton seed and pea-nut oils for the margarine makers. If this plan is successful it may double the consumption of cotton-seed oil in the margarine industry. The Norwegian firm will purchase the best grades of cotton-seed and pea-nut oils, and will also harden on toll.

During the past five years great progress has been made in the hydrogenation of liquid oils, by which process these oils are chemically transferred from the "unsaturated," or liquid, series to the "saturated," or concrete series. Theoretically the process is simple, consisting merely in adding two atoms of hydrogen to the oil molecule; but the means for accomplishing the result have been complicated and expensive, though now growing more simple.

Edible fats with high melting-points are higher in price than the others. Hard fats are needed for making hard soaps, and artificial lard and butter, and the present natural supply is not adequate. Some apparently successful work is now being done on a comparatively small scale in the United States in hardening cotton oil for artificial lard, and in Europe several plants are operating on various oils for soaps and candles. Many European margarine factories are experimenting on hardening cotton and pea-nut oils to replace copra oil, which is now very popular and high in price.

Some criticism has been directed at the use of hardened oils for edible purposes on the ground that nickel is used in the process, but the manufacturers say that although nickel is generally used none of it is left in the oil, and that even if it were it is harmless, as shown by many tests with animals and with human "poison squads."—*Chemical Engineer*, xix., No. 1.

ENZYMES OF *ASPERGILLUS ORYZAE* AND THE APPLICATION OF ITS AMYLOCLASTIC ENZYME TO THE FERMENTATION INDUSTRY.

By JOKICHI TAKAMINE.

History.

ASPERGILLUS ORYZAE, an insignificant species of fungi, belonging to the genus *Aspergillaceae*, plays an important rôle in the national economy of Japan, on account of the particular enzymes it generates during its growth. Other species of the same genus are also largely employed for production of various dietary articles in almost all countries of the Orient besides Japan. Nevertheless, its utilisation in Occidental countries is singularly lacking. Calmette and Bodin's investigation on amylomyces, with a view to utilising it in the spirit industry, is an isolated instance in Europe, and their process, known as the amylo-process, has been in operation in France since 1891.

In 1891 I made an arrangement with the Distilling and Cattle Feeding Co., of Peoria, Ill., and carried out on a practical scale the application of the *Aspergillus oryzae* to the American Distillery. My experiments, which ran for a couple of months on a 2000-bushel scale at the Manhattan Distillery, were partially successful, but, unfortunately, the process did not attain general recognition of its merit because it still lacked means to overcome various impediments due to trade conditions and difficulties in adapting the process in the new field of application. I did not forsake the investigation after this first trial, but became even more enthusiastic about perfecting the method. Improvement after improvement was added, and I now believe that I can soon demonstrate its usefulness.

For many years *Aspergillus oryzae* has been employed in Japan for varied purposes. Sake, or rice beer, soy, and miso are the products which are made by the use of this fungus. The fermentation of sake for the fiscal year of 1912 contributed to the national treasury the goodly sum of 41,974,630 dols. revenue. The tax on the production of soy (bean sauce) amounted to 2,048,141 dols. The total cost of both and other articles produced by aid of the fungus in question is put at an aggregate of 200,000,000 dols. It will thus be seen how important a rôle the fungus is playing in the national economy of Japan. If we add to the above statement the products and cost of the articles which are put out through the useful services of this fungus, or other species, rendered in all the countries of the Orient, the grand total is an enormous amount. Curiously enough this tiny and important hustler has scarcely attracted attention in the Occident, and this fact made me determine to work for its introduction to industrial use in the United States.

Scientifically, *Aspergillus oryzae* has attracted the attention of Occidental investigators as far back as 1875. Professor Kozai, of Tokyo Imperial University, reviewed the literature regarding the early investigations on the subject of *Aspergillus oryzae* and its industrial applications (*Centralb. f. Bakteriologie*, 1900, vi., No. 12), and gives credit to Hoffmann and Korshelt as the first writers upon the subject. Korshelt made an important contribution to the knowledge of the fungus in Europe (*Mittheilungen deutschen Gesellschaft f. Natur und Völkerkunde Ostasiens zu Tokyo*, Heft 16). His report was upon sake fermentation, with special reference to an amyloclastic enzyme which occurs in the culture of the fungus on rice, and which he named Eurotius. In his "Chemistry of Sake Brewing" Atkinson discusses the function of the enzyme just named. The fungus was then known as *Eurotium oryzae*, being first identified by Ahlburg in 1876, but Cohn's later investigation led to renaming it *Aspergillus oryzae* ("Wakreobericht der Schleisiochen Gesellschaft f. Vaterl.," Kulter., 1883, Bd. Ixi., p. 226). It was re-examined by Bosgen, Schröter, and later Wehmer, who gave full morphological descriptions of it.

O. Kellner and his pupils' investigations on invertase, amylase, and maltase are worthy of note. Controversies then existed with regard to the function of *Aspergillus oryzae* in sake fermentation. It was thought, on the one hand, that the conidia (spores of the fungus) may transform, under certain favourable conditions, to peculiar yeast cells, whose action induces the saccharified mash of rice to sake, containing 10–15 per cent alcohol. Korshelt propounded this theory, but was opposed by Atkinson. I myself confess that I shared the same view with Korshelt, but later was led to abandon it. Juhler, confirmed by Jorgensen (*Centralb. f. Bakteriologie*, II., Bd. I., pp. 16, 326) and Hansen (*loc. cit.*, p. 65), also gave opinions agreeing with the transformation theory. Kozai and Yabe (*Centralb. f. Bakteriologie*, II. Abt., Bd. I., p. 619) showed that *Aspergillus* and *Saccharomycetis* have nothing in common. Klocker, Schioning, Seiter, and Sorrel finally established the error of the transformation theory.

Acclimatisation of Aspergillus oryzae.—For a few years I have been working on acclimatising *Aspergillus oryzae* to various kinds of antiseptics. The art of acclimatising fungi to antiseptics is not new, e.g., the growth of yeast in a medium containing fluoric acid or other antiseptics has been tried and also put into practice. Effront's attempt to increase fermentation products in the distillery by means of his process is well known. It consists of acclimatising yeast to hydrofluoric or some other inorganic acid, and then employing it in a mash containing the acids, so that yeast can multiply without being disturbed by the various bacteria which gradually infect the mash. So far as I know, nobody has yet tried to acclimatise *Aspergillus oryzae* for practical purposes. This is because the utilisation of this interesting fungus is very little known, or is ignored in the United States and Europe, while the use of antiseptics is rather unnecessary in the fermentation industry of the Orient, since it prefers mixed culture to the pure, on account of the flavour or bouquet of products still thought to be imparted from a mixed culture.

Since my object in producing the culture of *Aspergillus oryzae* is chiefly concerned with the utilisation of its amyloclastic property developed during its growth and multiplication, it matters little whether the culture medium employed contains antiseptics or not, provided I can get the culture which is possessed of maximum enzymic function. To the growth of *Aspergillus oryzae* on wheat bran as a culture medium I gave the convenient name of "Taka-Koji," and have employed it for a number of years to distinguish it from that known in Japan as "Koji," which is a culture on steamed rice.

Taka-Koji is designed for a substitute for malt as an amyloclastic agent in varied fermentation and other allied industries. Its proposed use is encouraged by the fact that the cost of malt is subject to fluctuations, according to the crop conditions of barley, while bran is exempt from similar market conditions. Besides, the transformation of bran into Taka-Koji can be accomplished in forty-eight hours, while malting needs three or four times as long for completion of the process.

The making of Taka-Koji, as it was formerly practised, was described by myself some years ago before the New York Section of the Society of Chemical Industry (*Fourth. Soc. Chem. Ind.*, Feb. 28, 1898). Later, several improvements were made, and quite recently a radical departure was made in the mode of effecting the culture. I will, however, describe briefly the process as practised some years ago, so as to facilitate my exposition of the subject-matter.

The process consists of first moistening and then steaming wheat bran, so as to sterilise the material and at the same time to gelatinise the starch. After cooling the steamed mass down to 40° C., a small quantity of the spores of fungus are intimately mixed with it. It is now carried into a room where the floor is cemented, and spread in a thin layer of about 1½ inches thick. It is still better if put

into a number of trays with wood or metal frames, and provided with a false bottom of wire netting, fine enough to hold the particles of bran. The layer can be made in this case a little thicker, since air supply can be obtained from both top and bottom. Such trays are placed upon a specially constructed rack, to hold the trays one above the other, and about 2 inches apart. The temperature of the room is kept at about 30° C. at the beginning by means of opening steam jets direct into the space. This also keeps the room moist and warm. Within sixteen to eighteen hours the fungus commences to multiply, which action is easily followed by the gradual rise in temperature in the room. From this time on steam is turned off gradually, and at last entirely shut off. After twenty to twenty-four hours from the time of inoculation the growth and multiplication of the fungus becomes so vigorous that it is necessary to cool the room by the introduction of fresh, cool air. Carbon dioxide resulting from the vigorous growth of the fungus becomes very conspicuous, and the room needs the renovation of air which is effected by the air draught introduced for cooling purposes. Care should be taken that the air is supersaturated with moisture, so that the culture medium can always be kept from drying. The temperature of the room often goes up as high as 40–42° C. As long as the growth of fungus is comparatively pure and the mass is kept moderately moist to furnish the necessary amount of water for the culture, such a high temperature does not interfere with the generation of amylolytic enzyme in fungus cells and its secretion into the medium. The optimum temperature of the fungus growth lies, however, between 30–35° C. It is, of course, desirable to keep the temperature as nearly as possible between these limits. For eight or ten hours the multiplication of fungus is most vigorous, and there high temperature prevails. Then a gradual decrease in temperature is noticed until the culture medium is replete with the mycelia of fungus within forty-eight hours from the time of inoculation. At this point vigorous and numerous conidiophores are already to be seen with yellow or greenish yellow conidia (spores). The diastatic strength of Taka-Koji has now reached its maximum, and the Taka-Koji is ready to be taken out for use. When the vigorous growth of fungus has ceased, the medium is liable to be easily infected with injurious bacteria, which may destroy the diastase already generated. It is, therefore, necessary to conduct dry air into the room where Taka-Koji is manufactured, so that it shall be dried and made exempt from destructive infection. When the moisture of Taka-Koji is reduced to 10–15 per cent, it is immune from infection of bacteria, and can be kept for several months. By use of antiseptics, such as formaldehyde, benzoic or salicylic acid, bacterial infection of Taka-Koji can be easily avoided.

While mould fungi in general can tolerate quite a quantity of antiseptics, nevertheless, if they are acclimated to same, such toleration will attain to a conspicuous degree. One part or formaldehyde to 2500 parts of a culture medium does not considerably hinder the development of fungus. As to benzoic or salicylic acid, 1 part to 300 parts of a medium is almost immune to fungi. I had *Aspergillus oryzae* acclimated, and the result of using it enabled me to obtain Taka-Koji 100 per cent stronger in amylolytic power than the product obtained by the old process.

Drum Experiments.

Encouraged by this result, I thought of growing the acclimated fungus on the culture medium placed in a cylinder similar to a pneumatic malt drum. This is not a new idea. I carried out a series of experiments nearly twenty years ago, but then without the use of the acclimated variety of *Aspergillus oryzae*. My experiments were then a total failure, which made me think the fungus could not grow on the material in motion. If we consider the case of sprouting barley in a pneumatic drum it is, of course, seen that the development comes from within, where the vitality of the seed resides; hence the slight

impediment, due to frictions between the moving mass, is not sufficiently severe to totally inhibit the sprouting of the grains. The case is different when the fungus is grown on the culture medium in motion, since it must develop and multiply where frictions must always be injuring delicate mycelial cells of fungus. In my early experiments it was noticed that the fungus shows an initial growth indicated by the rise of temperature, and also observed under the microscope, but it gradually retrogrades. Meanwhile, bacterial infection sets in and totally destroys the fungus growth.

The subject, once almost forgotten, returned to my mind as I said above, and I decided to repeat experiments again. A small experimental cylinder, revolving a few times per minute, was made out of a Mason jar and clock mechanism. About 30 grms. of steamed bran were put in it and mixed with the new variety of acclimated fungus, and the whole was kept in an enclosure maintained at 30° C. Unexpectedly a fair result was obtained, in which I noticed a very interesting fact, namely, one side of the bran particle is covered with the fungus. It is the inner side of the bran. This side is coarse in structure and is rich in starch and protein matter. If the bran is moistened and steamed, this particular side shows a tendency to curl inward, and assumes the shape of pericarp previous to its severing from the kernel. When each particle of the bran has curled, the inner side is naturally protected from the friction between particles when they are put in cylinders and motion is imparted to the mass by revolution.

My success and observations encouraged me to construct larger apparatus for 100 grms., 1 kilo., 5 kilos., 20 kilos., and finally 70 kilos. capacity. I was very glad to confirm in every experiment my belief that the process of making Taka-Koji in a pneumatic drum is feasible. Therefore, I ordered a drum of about 4800 lbs. capacity for Taka-Koji manufacture, which is the size for an 8-ton malt drum. In this drum many new devices were introduced, but, to my grief, such elaborate devices became in fact stumbling-blocks, and the experiments were far from successful. The new devices were taken out one after another until at last the drum remained as simple as that of my own laboratory make. At length, after repetitions of more than fifty experiments, I was enabled to obtain a fairly good outcome, and was able to show that the process could be accomplished successfully on a large scale. The first drum became so dilapidated from the alterations and changes that I had to order the second apparatus. It is now ready, and I am soon to try it out. Its success is hardly to be doubted.

The drum consists of a huge, plain iron cylinder, provided with inlet on one side and outlet on the other, through which air can be passed by means of a suction fan located on the outlet side. The apparatus is furnished with mechanism to turn the cylinder at the rate of once per minute. An iron pipe runs through the centre of the cylinder independent from it. It branches out in several places along the whole length, each branch ending in a spray nozzle, through which water or steam can be turned upon the material. The Koji manufacture in this drum is carried out as follows: The wheat bran is dumped in, then the necessary quantity of water, and finally the steam is added, the mass being put in motion by revolution of the drum. As soon as the mass is properly steamed, it is cooled to 45° C. cool moist air. Into this mass an aqueous solution of antiseptics, and then spores of the fungus suspended in water, are sprayed. The temperature of the mass is generally at 38–40° C. The drum is now brought to a standstill, and left for about twelve hours, when the gradually decreased temperature again commences to go up. This means initial growth of the fungus. The drum is now put in motion, and a slight air current is passed over the mass, care being taken that the temperature should not be lower than 30° C. At the eighteenth hour the temperature shows a tendency to rise quickly, and at the twenty-fourth hour it reaches its maximum. The force of the air current is increased

accordingly to keep the temperature at about 38° C. A suction pump of 1600 to 1800 cubic feet capacity per minute was put in full action, yet the mass of 2400 pounds was barely within the limit of 38° C. According to my small experiment, a higher temperature of 42° C. did not impair the diastatic activity formed by the growth of the fungus; but if it is kept within 40° C. it is so much better for the process, that the air is previously cooled and saturated with moisture by drawing through a freely sprayed coke tower. In forty-eight hours the process is concluded.

The Taka-Koji manufactured in the drum is more compact and glossy than that grown otherwise. The inward side of the bran is covered with a felt-like growth of mycelia which do not branch out many conidiophores bearing spores; hence the colour is whitish.

The labour needed for this process is reduced to one-sixth of that necessary in the old process. The saving of space is also considerable and the quality of Taka-Koji is excellent. Thus the process promises well for furnishing a substitute for malt in alcoholic fermentation and other industries, where amylolytic enzyme is required.

Dr. Niels Ortvad, chief chemist of Hiram Walker and Sons, of Walkerville, Ontario, Canada, kindly carried out a series of experiments in his distillery, and published his results in his paper contributed to the last Congress of Applied Chemistry, held here in New York. To quote briefly, he said:—

"On account of the numerous great variations in the price of barley malt (in two consecutive years the price varied 100 per cent), it would be of great value to the distilling industry if a converting medium of moderate and more uniform price could be employed instead of barley malt. Eliminating therefore the different grains as a source of converting medium, I turned to the diastase produced by a micro organism, the *Aspergillus oryzae*. Takamine was the first to introduce the Koji process in America. As far back as 1889 he advocated the use of Koji in the distilling industry. Instead of growing the fungus on rice, Takamine employed a material far cheaper for this country, namely, wheat bran. An extract of the wheat bran, on which the *Aspergillus oryzae* had been allowed to germinate, contained the diastase, produced by the *Aspergillus*, and this extract was mixed with the mashed grain, bringing about the conversion of the starchy materials. Lately, I understand, he has succeeded in adapting a modification of the Galland-Henning malt drum system to his process. This should be a great improvement over the old floor system, in so far as it makes it possible to work under absolutely sterile conditions. For my experiments I decided to use the Taka-Koji itself instead of the diastatic extraction of same and add it to the mash in the same way as malt. Before beginning the practical experiments in the distillery, laboratory experiments were conducted on a small scale to ascertain the amount of Taka-Koji which was necessary to convert a certain amount of starch into sugar, and also the optimum temperature at which to conduct the conversion. It was found that 4 grms. of Taka-Koji was sufficient to give a complete conversion in a mash made from 96 grms. of corn and rye, the corn containing 15.0 per cent of moisture and the rye 14.0 per cent. Three experiments were made in the distillery. For the first experiment only a 14 gallon can was used, and a portion of our ordinary mash from the mash-tub was employed, the mash being taken from the main mash just before malt was going to be added for conversion. The second experiment was performed on a somewhat larger scale. Instead of using mash material from the mash-tub, the mash was made separately. It consisted of 500 kgrms. altogether, of which 20 kgrms. were Taka-Koji. The third experiment was performed on a good-sized working scale. Two mashies, each consisting of 3401.94 kgrms. (of which 131.5 kgrms. were Taka-Koji), were prepared. The two mashies were filled in Turn No. 25 of Friday, May 26, 1911. Turn No. 25 was distilled separately, and the yield

was 36 litres of 100 per cent alcohol per 100 kgrms. of mash material, just a trifle higher than the yield of the other mashies which were made the same day. In judging the adaptability of Taka-Koji for use in distilleries several questions must be asked and answered:—

"Is Taka-Koji capable of giving a complete conversion of the starchy materials in the mash?"

"Yes, 4 per cent of the air-dried Taka Koji will in fifteen to twenty minutes give a complete conversion of well prepared mash material.

"Is the fermentation a satisfactory one?"

"While it is accompanied by a strong odour, which is prevalent in the fermenting room, the fermentation, however, is very rapid and complete, and on this account should give rise to the least amount of infection.

"Is the yield of spirit satisfactory?"

"Yes, the yield obtained was a little higher than the yield gotten from the barley malt mashies, although the total fermentable extract available in the mash material was less. The yield of 36 litres of 100 per cent alcohol per 100 kgrms. of mash material is, of course, only a comparative yield. In distilleries which employ cookers and boil the corn under pressure, a higher yield would naturally result.

"Therefore I should say as a final conclusion that in distilleries which make commercial or potable neutral spirit, the Taka-Koji process could be introduced to advantage. Aside from a probable higher yield in spirit, the saving in malt bill would be worth while in years with normal malt prices, and very considerable in years when the malt prices become abnormal."

Taka-Diastase.

An aqueous extract from the Taka-Koji can be easily made by percolation and an enzyme can be precipitated by adding alcohol to such extent as to contain 70 per cent by volume of same in the mixture. The precipitate is dehydrated by means of strong alcohol, dried and powdered. It is a white or yellowish white powder of hygroscopic nature. It is marketed in this form for medical use under the name Taka-Diastase.

Though known as an amylolytic agent, it contains various enzymes; nevertheless, amylolytic and proteolytic enzymes predominate. O. Kellner and his pupils early reported the presence of invertase maltase beside amylase (*Zeit. Phys. Chem.*, xiv., Part III.). Newcombe established the presence of cyase (*Annals of Botany*, 1889, No. 49), while Aso reports, in a Bulletin of the Agricultural College of Japan, the presence of oxydase in Koji extract. According to Brunstein, Koji contains an emulsin-like substance that decomposes helicin into salicylic aldehyde and glucose, which former is later oxidised into salicylic acid; amygdalin is decomposed into cyanhydrin and glucose, which former is later oxidised to mandelic acid.

Investigations on peptase and ereptase carried out by S. H. Vines are replete with interesting observations (*Annals of Botany*, 1910, xxiv., No. 93). He found that Taka-Diastase contains the above enzymes and effected the separation of one from the other. By treating Taka-Diastase with 50 per cent ethyl alcohol and leaving it over forty-eight hours ereptase went into solution while peptase remained behind. Equally valuable and interesting are researches of J. Wohlgemuth (*Biochemische Zeitschrift*, xxxix., Parts III. and IV.). He states that Taka-Diastase contained an enormous amylolytic function; the valuation of same according to his method showed to be $D_{38}^{24} h = 62,500$ ("D" Diastatic power digested at 38° C. for twenty-four hours). Testing tryptic action of Taka-Diastase he found that 1 grm. corresponds to nearly 100 cc. of the pancreatic juice of man as well as dog; hence he recommended the use of Taka-Diastase for therapeutics in cases of general debility. Wohlgemuth also proved the presence of maltase, chimosin, ereptase, and lipase in Taka-Diastase.

Quite recently, Kita reports the discovery of a specific

enzyme in Taka-Diastase or in a Koji extract, whose function is to transform starch direct into glucose (*Journ. Ind. and Eng. Chem.*, 1913, v., 220). He doubts very much the opinions entertained by preceding investigators that Taka-Diastase first transforms starch to maltose, and that the latter is converted to glucose by the action of the maltase present. His experimental data have not yet been confirmed by any other experimenter. Such an enzyme as Kita reports probably exists, but confirmation by more exhaustive proofs than he has furnished must be had.

The resistance of amylolytic enzyme of Taka-Diastase toward acid is reported by many investigators. This fact becomes very significant when applied to the practical conversion of grain mash. In a grain mash where 10 to 15 per cent sugar is to be finally produced an addition of mineral acid, say, sulphuric acid, to an amount of 1 part to 2000 parts of mash accelerates the diastatic action at least 10 to 15 per cent. An equivalent of hydrochloric acid gives a similar result. Malt diastase is entirely inactive with such a high percentage of acid in mash.

Taka-Diastase possesses an important property as a medical agent; i.e., it is more stable than the diastase of malt. The latter loses its activity gradually, and within several months its activity dwindles, while Taka-Diastase remains almost unchanged for several years. How this stability is imparted to it is a subject full of interest for investigation. Taka-Diastase contains generally 10 to 15 per cent of ash; this can be reduced to 4 to 5 per cent by re-precipitations, but the activity of the enzyme does not increase even by this apparent purifying process, but, on the contrary, a loss of activity is occasioned in most cases.

The author extends his thanks to Mr. Wooyenaka for his untiring and valuable assistance, and to Parke, Davis, and Co., for affording every facility for carrying out the "Drum Experiments."

THE RADIUM : URANIUM RATIO IN CARNOTITES.*

By S. C. LIND and C. F. WHITEMORE.

I. Introduction.

THE constancy of the ratio of radium to uranium in the uranium minerals, and its significance in the theory of the origin of radium, have been recognised for some time. For its experimental demonstration we are indebted to the early work of Boltwood (*Phil. Mag.*, 1905, ix., 599; *Am. Journ. Sci.*, 1904, xviii., 97; 1908, xxv., 269), Rutherford (*Am. Journ. Sci.*, 1905, xx., 55; 1906, xxii., 1), Strutt (*Proc. Roy. Soc., A*, 1905, lxxvi., 88, 312), McCoy (*Ber.*, 1904, xxxvii., 2641; *Journ. Am. Chem. Soc.*, 1905, xxvii., 391); and Eve (*Am. Journ. Sci.*, 1906, xxii., 4).

At a somewhat later period it began to be recognised that certain uranium minerals of secondary origin, of which autunite, $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, is one of the chief representatives, show a ratio below that of pitchblende. In 1909, Mdlle. Gleditsch (*Comptes Rendus*, 1909, cxlviii., 1451; cxlix., 267) announced that she had found a sample of French autunite showing only about 80 per cent of the normal ratio. A low ratio was confirmed in 1910 by A. S. Russell (*Nature*, 1910, lxxxiv., 238), who, also in a sample of French autunite, found only 27 per cent of the normal ratio, while Soddy and Pirret (*Phil. Mag.*, 1910, xx., 345; 1911, xxi., 652), about the same time, found a sample of Spanish autunite with 44.5 per cent of the pitchblende ratio.

To account for these low ratios in a sense consistent with the Rutherford and Soddy theory of radio-activity, two different explanations have been proposed. The first

supposes that the secondary minerals are too young for the quantity of radium to have accumulated to the maximum equilibrium value shown in the older minerals such as pitchblende. The second mode of explanation assumes that the secondary minerals, owing to a looser mechanical structure, are more subject to a leaching process by water, and that radium is more readily removed than uranium, which results in a low ratio of the former to the latter.

Additional evidence, adduced principally by Markwald and Russell (*Ber.*, 1911, xlv., 771; *Jahrb. d. Radioakt. u. Elektronik*, 1911, viii., 457), appears to support the "leaching" theory, since the ionium:uranium ratio was found much more nearly to approach theory in autunite than does the radium:uranium ratio, thus indicating a removal of radium, while lead, one of the end products of the uranium family, was found to be almost entirely lacking.

At the same time that Mdlle. Gleditsch (*loc. cit.*) announced the existence of a low radium:uranium ratio in autunite, she reported a high ratio (about 16 per cent high) in thorianite of Ceylon. The explanation of a high ratio appeared to present much more formidable difficulties than the low ones. Mdlle. Gleditsch favoured the view that either ionium, or some other unknown member between uranium and radium, had a much longer period than previously supposed, necessitating a greater relapse of time for equilibrium to be attained. Consequently all the uranium minerals according to this view would be slowly advancing to an equilibrium quantity of radium higher than that in most pitchblendes.

The view of Mdlle. Gleditsch's did not find general acceptance. Soddy and Pirret (*loc. cit.*) had also examined autunite, pitchblende, and thorianite; and while confirming a low ratio for autunite, as already stated, they failed to find a difference between the latter two exceeding 3 per cent, which they regarded as within their limits of experimental error.

In a later investigation extending to a much larger number of uranium minerals Mdlle. Gleditsch (*Le Radium*, 1911, viii., 256) confirmed her earlier results, finding ratios of radium:uranium varying from 1.82×10^{-7} for chalcotite of Saxony, to 3.74×10^{-7} for pitchblende of Cornwall; while from two pitchblendes from Norway she reported 3.48×10^{-7} and 3.64×10^{-7} , respectively.

The most recent experimental contribution to this subject is the searching examination by Heimann and Markwald (*Jahrb. d. Radioakt. u. Elektronik*, 1913, x., 299; *Physik. Zeit.*, 1913, xiv., 303) of the radium:uranium ratio in eight samples from all the principal pitchblende localities of the world, including Joachimsthal, Saxony, German East Africa, Norway, Bohemia, Colorado, and Cornwall. Determinations were made by two entirely different methods, the emanation method and the gamma-ray method. In all eight samples constancy of the radium:uranium ratio was found within 0.4 per cent. The absolute value of the ratio was determined by comparison with a radium solution having its origin in the Hoenigschmid (*Sitzb. Vienna Acad.*, Abt. II.a, Nov., 1911, cxx.) atomic weight radium of the Institute for Radium Research in Vienna and was found to be 3.328×10^{-7} . The satisfactory agreement of this number with the theoretical value of the ratio is calculated from radiation data (see calculation by Stefan Meyer, *Ibid.*, cxxii., June, 1913), lends it a great degree of reliability.

Carnotites have been included among the specimens of uranium minerals examined by a few authors. From the results of Boltwood (*loc. cit.*) and of McCoy (*loc. cit.*), no abnormally low ratio for this mineral was apparent, while Mdlle. Gleditsch (*loc. cit.*) reported, for a sample of Colorado carnotite, a ratio of only 2.34×10^{-7} , which corresponds to about 70 per cent of normal ratio. Markwald and Russell (*loc. cit.*) found 91.6 per cent of normal ratio for a carnotite of Colorado and 71.5 per cent for one of Florida (?). From these results the impression seems to have been general that carnotite always has a low ratio.

* Published by permission of the Director of the Bureau of Mines, U.S.A. From the *Journal of the American Chemical Society*, xxxvi., No. 10.

The increasing importance of carnotite as one of the chief sources of radium has made it appear desirable to undertake a thorough examination of the radium:uranium ratio in a much larger number of samples of this mineral. To this end about twenty specimens of carnotite of all grades and from various localities have been examined. By way of anticipation, it may be stated here that, on small samples, we have confirmed in some cases the low ratios, finding one almost as low as that of Mdle. Gleditsch, which is to be regarded, however, as very exceptional. On the other hand, we have also found an equal number of high ratios (also in the case of small samples only), some as high as the highest ratios found by Mdle. Gleditsch for any of the primary minerals and one considerably higher, 4.6×10^{-7} , which is the highest ratio yet reported for any uranium mineral.

What appears to us to be of the greatest significance is the fact that these abnormal ratios, both high and low, occur only in samples representative of small quantities of ore (a few pounds), while all samples from large lots (one ton up to a carload) invariably show a ratio practically identical with that of pitchblende. This appears to us to suggest strongly a theory of transposition within the ore bed rather than one of complete removal by leaching. This point will be more fully discussed in the Conclusion; but it is quite evident that there is no reason to suppose carnotite to be abnormal in ratio, provided the determination be made on a sample representative of a considerable portion of an ore bed, while rather large deviations in both directions are found by the examination of small samples.

II. Carnotite Samples.

The samples of carnotite investigated have been chosen with the object of representing the principal localities in Colorado and Utah where this ore has been found in any quantities of importance. All grades of carnotite from 1.5 to 33 per cent of U_3O_8 have been included.

The samples were not collected by the authors, nor were they taken with any reference to geological conditions or position in ore beds, but are simply representative of carnotites as they come on the market either as specimens or in commercial quantities. As already mentioned, a special significance attaches to the specimens representative of large quantities of ore. Owing to the magnitude of the present production of carnotite ore we have been fortunate in obtaining ground samples representing large quantities of carefully sampled ore which we feel is of the utmost importance in obtaining correct values for radium content. We wish to take this opportunity of thanking all the gentlemen through whose courtesies we have been supplied with these samples.

III. General Discussion of Methods.

Two distinct determinations enter into the radium:uranium ratio which contribute equally to the accuracy of the result. The methods of determining radium in carnotite differ little from those employed for many other uranium ores and present no especial difficulties, provided suitable methods are used to liberate the emanation. We have employed the emanation method exclusively and always after attainment of equilibrium in the samples, sealed in glass tubes for a month or more; accumulation methods starting from zero emanation have not been used. Aluminium leaf electrosopes of the Wilson type were used with discharged chamber and leaf system separate. Calibration was made by means of analysed pitchblende from Colorado assuming the ratio found by Heimann and Marckwald of 3.328×10^{-7} to be correct (*loc. cit.*).

The determination of uranium in carnotite does present, however, exceptional difficulties owing to the presence of vanadium, and many of the earlier proposed methods of separation have been found unsuitable. Full details of the method which we have found satisfactory are given in Section VII, as well as references to other methods which we have employed in some cases for control.

The low uranium content of most carnotites as compared with other higher grade ores renders it difficult to attain the desired degree of accuracy in determining the uranium and, to a less extent, the radium content. We have sought to overcome this difficulty by repeating determinations frequently and by employing additional methods of control in all cases of doubt. These same precautions have also been used in the radium determinations, which have all been checked by two independent methods of liberating the radium emanation. Especial care has been taken in the case of all abnormal ratios to be sure that the deviations were real ones and not due to errors in the measurement either of radium or uranium. We believe that the average results reported in Sections VIII. and IX. are accurate to within 1–2 per cent.

(To be continued).

POTASH SALTS.

SUMMARY FOR 1913.*

Compiled by W. C. PHALEN, United States Geological Survey,
Washington, D. C.

THE activities of the United States Geological Survey in the investigation of potash salts during 1913 were more restricted than in previous years. In the field, drilling was carried on in two areas, Columbus Marsh and Black Rock Desert, Nevada, but it was of short duration, owing to the inaccessibility of the area for an unusually long period of the year, on account of the heavy rains, which made it impossible to transport apparatus to the drill sites. A general plan involving the stratigraphic study of the so-called "red bed" salines of certain of the South-Western States, including New Mexico, Arizona, and Utah, was begun by N. H. Darton, and several months of field work was done. A brief review of certain basins in the Great Basin region of California and Nevada was made by H. S. Gale in the further general study of the hypothesis that potash deposits may be found in desiccated lake basins.

In the laboratory, attention has been directed to a few definite problems indicated by the preceding general experimental work.

POTASH SALTS IN THE GREAT BASIN REGION.

Deep Drilling Explorations.

In addition to the drilling explorations carried out by the Survey and mentioned in the introductory paragraph, the Railroad Valley Co., of Tonopah, Nev., did some deep drilling during the year. Since this company began operations, more than two years ago, it has drilled more than 10,000 ft. in seven wells located in Railroad Valley, Nye County, Nevada.

During July, 1913, the company in its well No. 2 encountered buried soda-bearing beds made up chiefly of the mineral gaylussite, $NaCO_3 \cdot CaCO_3 \cdot 5H_2O$. These were penetrated a distance of 127 ft. without reaching bottom. Since potash salts are more soluble than the mineral gaylussite, they would in a normally deposited saline series overlie that mineral. On this basis it was assumed that they did overlie the gaylussite in some other part of the basin, namely, in the deepest part, in which, consequently, they would cover a smaller area than the gaylussite deposits. In the work the gaylussite bed was counted on as furnishing a datum plane to aid in tracing the contours of the basin, and hence in locating the deepest part in which the potash salts were expected to be found. Proceeding on this hypothesis, four additional wells were drilled, but without conclusive results. Two of these wells did not encounter the gaylussite deposit at all. It was also found that the upper portion of the gaylussite beds was flatter and more variable than was expected—conditions which rendered precise correlation and determination of contours

* From *The Chemical Engineer*, xx., No. 3.

impossible. Operations on the seventh well drilled had to be suspended before it reached the depth at which the hoped-for data were expected to be obtained.

The gaylussite beds were encountered only in wells Nos. 2, 4, and 6. In No. 2 they were penetrated a distance of 127 ft., in well No. 6 a distance of 194 ft., and in well No. 4 a distance of only a few feet. In no well was the gaylussite drilled through, but it was found to be purer and more solid toward the bottom. The precise correlation of the two gaylussite deposits found—the one in well No. 2 and the other in well No. 6—was not considered possible, and it was also found impossible to establish synchronism between any two particular beds of wells No. 2 and No. 6. Still, there seems little doubt that the gaylussite series of wells No. 2 and No. 6 are synchronous and represent the same stage of concentration of the same saline solutions.

The most important question confronting the company at present is whether well No. 6 is in or near the deepest depression, or whether such depression lies an unknown distance to the south. This doubt can be settled only by further drilling. If such drilling indicated no southward extension of the basin, the chances of finding important segregations of potash salts are very slight. If it be proved that the basin does extend farther to the south, then probably several wells will have to be drilled to obtain some idea of its size and character and of the existence of other saline deposits in it.

In the event that no potash salts are found, it is possible that the gaylussite bed itself may be of value. The extent of this bed will have to be ascertained by drilling, and methods will have to be devised both for mining it and for producing soda from it.

The report of E. E. Free, consulting geologist to the Railroad Valley Co., from which these data were obtained, was transmitted January 2, 1914. This report contains, in addition to the information given, a map showing the location and records of the wells, together with an appendix describing gaylussite and its possible utilisation.

It is reported that the Nevada Potash Co., with headquarters at Goldfield, Nev., plans to explore Clayton Lake, 20 miles west of Goldfield.

Explanation of the Term "Potash."

To meet the numerous inquiries that have been addressed to the United States Geological Survey regarding the exact meaning of the terms "potash," "actual potash," and "potassium," the following explanation is given:—

The element potassium, represented by the symbol K, is the basis of all potash salts or compounds. This substance is a metal; that is, it possesses metallic properties. To prevent rapid change it must be kept from air and water, with both of which it combines with great avidity. Combined with oxygen it forms potassium oxide, represented by the symbol K_2O , known as potassa, but popularly as "potash." In estimating the quantity of potassium in the different products of the Stassfurt deposits, this compound, K_2O , is employed as a standard, the object being to establish a basis of comparison for all potassium salts. Among chemists as well as laymen there has grown up the practice of using for this standard the term "potash." When only the term "potash" is used in speaking of potash products, it is understood to refer to the potassium oxide (K_2O) present. As a matter of fact, however, potash salts are not sold in the form K_2O , but as the sulphate or the chloride (the chloride is also known in the trade by the chemically obsolete term "muriate of potash"). By the term "potassium sulphate" is meant potassium (K) combined with the acid radicle of sulphuric acid (SO_4), or potassium oxide (K_2O) combined with sulphur trioxide (SO_3), making the compound K_2SO_4 . By "potassium chloride" is meant potassium (K) combined with another element, chlorine (Cl).

In Table I. are given the percentages of the element

potassium and also the combination known as potash in or obtainable from the common potassium compounds and minerals.

TABLE I.—Potassium and "Potash" in Potassium Compounds.

Name and symbol.	Percentage of potassium (K).	Chemical equivalent = K_2O .
Element—		
Potassium, K	100	120
Potassium salts or "potash salts"—		
Pot. chloride (mineral sylvite), KCl ..	52	63
Pot. muriate (same as chloride) ..		
Pot. sulphate, K_2SO_4	45	54
Pot. nitrate (saltpetre), KNO_3	39	47
Pot. carbonate, K_2CO_3 (a)	57	68
Pot. hydrate or caustic potash, KOH ..	70	84
Pot. cyanide, KCN	60	72
Stassfurt minerals—		
Carnallite, $KMgCl_3 \cdot 6H_2O$	14	17
Kainit, $MgSO_4 \cdot KCl_3 \cdot H_2O$	16	19
Sylvite (potassium chloride), KCl ..	52	63

(a) The term "potash" is often applied to this compound.

DEVELOPMENT OF SALINE POTASH DEPOSITS.

California—Searles Lake.

A description of the saline deposits of Searles Lake, Cal., was published in this report for 1911 (H. S. Gale, "Potash Salts," U.S. Geol. Survey Mineral Resources, 1913, Part 2, p. 884).

Searles Lake, known also as Borax Flat, is a dry lake basin much like many other desert basins in the Western arid region. It is a broad, somewhat circular valley or depression lying between the Slate and Argus ranges in the extreme north-western part of San Bernardino County and near Kern and Inyo Counties. The camp known as the Borax is about 25 miles by road from Searles post-office, formerly Garden station, near the Mohave-Owenyo branch of the Southern Pacific Railroad. Searles Lake at present may be reached by the regular stage that runs from Johannesburg by the way of Garden station, or Searles, to Searles Lake, and thence on to Ballarat and Skidoo.

Searles Lake for many years was an important source of borax. Later the California Trona Co. was organised to produce soda ash from the deposits, and the lake has now become of interest in connection with the contemplated exploitation of its potash-salts deposits.

The announcement of Searles Lake as a possible source of potash-salts was made as a result of the collection and analysis of a set of brine samples from it in March, 1912, by E. E. Free, then of the United States Bureau of Soils, and Hoyt S. Gale, of the United States Geological Survey. A notice was at that time given to the press stating that reports which had been received concerning the unusually high potash content of the brine in this deposit were apparently confirmed by the results of these tests. Analyses of six brine samples taken at considerable depth in old wells at points distributed over the main salt flats showed that an average of 6.78 per cent of the total dissolved salts was potash (K_2O), corresponding to 10.73 per cent potassium chloride (KCl). The individual results obtained were 7.63, 6.23, 6.89, 6.06, 7.27, and 6.57 per cent. The uniformity of these results seemed to indicate, although it did not prove, homogeneity in composition of the brine throughout the salt deposit. Based in part on the logs of the wells that had already been drilled, a statement was also made at that time that "existing data give reasonable assurance that the brine-saturated salt body is at least 60 feet thick and covers an area of at least 11 square miles. On the assumption that the salt constitutes 25 per cent by volume of the brine, the total amount of potassium oxide available is estimated as over 4,000,000

Short tons (equivalent to approximately 6,000,000 tons of potassium chloride). This estimate is based on income plate data, but it is believed to be conservative."

During the year 1913 the American Trona Co. was incorporated to operate works for refining and marketing the different saline constituents of the Searles Lake deposits. It is proposed to spend 3,000,000 dols. in completing a railway from Searles to the lake and in building a plant to have a capacity of 2,000,000 gallons of brine a day.

Many deep drillings have been made at Searles Lake by the company, and the study of many hundred samples secured has enabled those in charge of the enterprise to devise a process for the treatment of the salines.

The new works will draw from the lake approximately one-tenth of an inch of brine a day; the natural evaporation is much larger, and varies from one-fourth to one-half of an inch a day. The plan of treatment consists in first precipitating the soda as the bicarbonate. The next step involves crystallisation in furnaces of simple type but large capacity. The process has been worked out with considerable care, but to insure against possible loss an initial unit with a capacity equal to 1 per cent that of the final plant will be erected and placed in operation before the main plant is built. It is expected that the daily output of the plant will be:—Borax, 225 tons; soda-ash, 508 tons; salt, 1507 tons; sodium sulphate, 593 tons; and potassium chloride, 489 tons. The company will depend for its revenue mainly on the potash salts, the soda ash, and the borax. The salt may ultimately be marketed, and it is possible that at some future time a use will be found for the sodium sulphate; but for the present these constituents are not taken into account (*Min. and Sci. Press*, June 14, 1913, p. 888).

According to the latest information, the experimental unit referred to above is nearing completion, and it is expected to be ready for operation in the latter part of 1914. The 31-mile railroad from Searles on the Nevada and California Railroad (Southern Pacific) is completed to the new town of Trona, where the new works are being built. It is expected that 20,000 gallons of brine will be handled daily at the new plant, and that the works will be enlarged at a later date. It is unlikely that the salts from the Searles Lake deposit will enter the market regularly until the latter part of 1914 (*Eng. and Min. Journ.*, xcvi., No. 9, 484, Feb. 28, 1914).

Oklahoma.

(L. C. Snider, Oklahoma Geol. Survey, 1913, *Bull.* 11, p. 213).

Common salt is found in what are generally termed "salt plains" in Oklahoma, that is, over broad areas in which incrustations of salt occur. This common salt has come from springs, which flow at particular places, or from saline ground waters, which permeate the soil below the saline crusts. Such saline ground waters may also have originated in springs with subterranean outlets. Most of the salt is supposed to have come from salt beds in the so-called "red beds."

One group of these salt plains is found in Jackson County. This group numbers three in all, lying close together on the west side of Sandy Creek, about three miles from its mouth and approximately the same distance south of Eldorado. The northern plain lies in the E. $\frac{1}{2}$ sec. 31, T. 2 S., R. 23 W., the middle one in the N.E. $\frac{1}{4}$ sec. 5, T. 3 S., R. 23 W., and the southern plain in the N.W. $\frac{1}{4}$ sec. 5 of the same township and range. All three plains are on small tributaries which flow north-east into Sandy Creek. The northern and southern plains are each about 100 yards wide and 400 yards long; the middle plain is only 40 yards wide, but is one-fourth of a mile long. The sandy floor of the plains is covered by a thin saline incrustation, and the water does not seem to be saturated.

The analyses of the soluble salts which have been made by the Oklahoma Geological Survey are not given in detail in the reference cited. According to Snider, the analyses

that have been made indicate the presence of much more sodium sulphate than sodium chloride; the potassium sulphate is also high. In the incrustation from the middle plain the proportion of sodium chloride is greater than in the two others, and there seem to be sufficient sodium and potassium sulphates to make the commercial recovery of common salt a question. It is possible that the potassium sulphate from the middle plain may be utilised as a by-product.

Texas.

(J. S. Udden, "Potash in the Permian Rocks of Texas," *Am. Fertilizer*, Dec. 14, 1912, p. 40).

In the search for a deep source of potable water at Spur, Dickens County, Texas, a deep well has been drilled by S. M. Swenson and Sons, of New York. The total depth of the well is reported as nearly 4500 ft. The upper 900 ft. of strata penetrated consist chiefly of red sand beds of shale, gypsum, and anhydrite, and two beds of rock salt, each about 10 feet thick and both more than 500 feet from the surface. Below the 900-foot level occurs a 250-ft. bed, consisting chiefly of fine sand, silt, and salt, the proportion of salt varying from 20 to 60 per cent. From the 1250-ft. level to the 2050-ft. level the character of the rock passed through his not known from samples, but is thought to consist chiefly of dolomitic limestone. Below this is found red silt or clay, dolomitic and shaly limestone, and anhydrite; then dolomitic limestone; then very pure anhydrite. At 3060 ft. a dark grey soft shale was met.

The presence of so much anhydrite and salt in the section led to the suggestion by J. A. Udden, of the Bureau of Economic Geology and Technology of the University of Texas, of the possibility of the presence of potash salts in the deposits. The well had in the meantime been cased below 1300 ft. A sample, however, was taken after the water had been baled to a depth of 2200 ft. This sample was examined by S. H. Worrell, also of the Bureau, with the following results:—

Analysis of Water from Well at Spur, Texas.

	Grains per gall.
CaSO ₄	1688.4
CaCl ₂	814.1
MgCl ₂	263.2
NaCl	4095.0
KCl	389.2
	7249.9

The potassium chloride, therefore, amounts to 6.65 grms. per litre, and constitutes more than 5.4 per cent of the total salts. As this amount of potash salts is somewhat high for a natural water, arrangements were later made for obtaining samples from different depths below the foot of the casing (1350 feet). Fourteen samples were next obtained and tested for potash salts, but in only one of them, namely, the sample from the same depth at which the earlier tests showed marked results in the content of potassium chloride, was any considerable quantity of potash salts again found, but the quantity found was approximately only one-third of that shown in the earlier sample. The results seem, therefore, to indicate the presence of a potash-bearing layer, bed, or stratum approximately 2200 feet below the surface in the well.

(To be continued).

Students' Roll of Honour.—The Manchester School of Technology possesses particulars of more than 550 students who were in attendance at the college during the academic year 1913—14, and who are now serving in various branches of His Majesty's Forces. With a view to the completion of a Roll of Honour, which shall also include the names of past students engaged upon military service, the Registrar will be glad to receive any information from such persons themselves or from their relatives or friends.

NOTICES OF BOOKS.

The Woburn Experimental Station. Report on the Field and Pot-Culture Experiments, 1913. By J. AUGUSTUS VOELCKER, M.A., B.Sc., Ph.D. London: John Murray. 1914.

THIS report contains the details of the field experiments of 1913, and also of the pot-culture experiments for the same year. The latter included the study of the influence upon wheat of various inorganic substances, e.g., zinc and copper salts, and also some work upon the effects of lithium phosphate and magnesia upon tomatoes. Experiments were also made upon the use of sulphur as a fertiliser, which were undertaken to test the conclusion reached upon the Continent—that it has a beneficial effect upon certain crops. The results were negative; dressings of from 3 to 12 cwt. per acre having no effect upon the weight of the crop obtained.

Annual Report for 1913 of the Consulting Chemist. By J. AUGUSTUS VOELCKER, M.A., B.Sc., Ph.D. London: The Royal Agricultural Society of England. 1914.

IN this report Dr. Voelcker discusses some general inferences which may be drawn from the results of the analysis of various samples submitted by the members of the Royal Agricultural Society, and draws attention to the quality of the feeding stuffs which are now being placed upon the market. Useful and thoroughly practical information as to the prices and relative values of different feeding stuffs is given, and farmers will find that the report will repay study. There has been a considerable increase in the number of soils sent for analysis, while the total number of samples for 1913 was about the same as for the previous year.

CORRESPONDENCE.

WAS IT PROPHETIC?

To the Editor of the *Chemical News*.

SIR,—In these strenuous times, when serious faces are the rule and smiles the exception, one may be excused for taking advantage of the chance to raise one of these, even though it be at the expense of your valuable journal. Looking into vol. xvii. of the *CHEMICAL NEWS*, p. 2, one finds the account of an explosive powder, regarding which it is said:—"The preference was given to the powder not only for its power . . . but alas for its economy . . ." Of course, also was the word intended, but it is one of the neatest of printers' errors that one could now come across, for explosives seem to be cheap in these days.—I am, &c.,

F. J. R. CARULLA.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clix., No. 8, August 24; No. 9, August 31; No. 10, September 7; No. 11, September 14, 1914.

These numbers contain no chemical matter.

No. 13, September 28, 1914.

Plurality of Amyloses.—Ch. Tanret.—When different kinds of starches are heated with water to different temperatures it is found that at any definite temperature very different quantities of amylose are dissolved. If the solubility curve of the amylose of any one starch is plotted, it is found to be very irregular, indicating either that it is a mixture of homologous amyloses of different solubilities, or else that the same principle is in different states of condensation. The author's experiments give a new proof of the plurality of amyloses.

Atti della Reale Accademia dei Lincei.

Vol. xxiii. [i.], No. 12, 1914.

Dehydration of Glycocol.—L. Balbiano.—If finely powdered glycocol is heated to 200–204° with excess of naphthalene the mixture becomes brown and finally black. When the excess of naphthalene is separated off it is found that the insoluble residue consists of the substance left when one molecule of water is subtracted from one of glycocol. With cymene the elimination of water is slower and less complete.

Oxyhalogenides of Lead.—G. Sandonnini.—The author has confirmed the existence of $PbBr_2 \cdot PbO$ at a high temperature and in the anhydrous state, and of $PbBr_2 \cdot 2PbO$. He has also proved the existence of a compound $PbBr_2 \cdot 4PbO$. Thus there is complete agreement in the behaviour of the chloride and bromide towards the oxide, and the compounds formed are of the same type. When, however, the compound $PbBr_2 \cdot 4PbO$ fuses it undergoes decomposition, while $PbCl_2 \cdot 4PbO$ fuses unaltered. In the system fluoride-oxide of lead no compounds are formed, but only a eutectic.

MEETINGS FOR THE WEEK.

MONDAY, NOV. 2nd.—Society of Chemical Industry, 8. Discussion on "The Present and Future of the British Chemical Industry as affected by the War."

WEDNESDAY, NOV. 4th.—Society of Public Analysts, 8. "Addition of Foreign Substances to Flour, with special reference to Persulphates," by A. R. Tankard. "Bleached and Unbleached Flour" and "Methyl Red as an Indicator," by R. T. Thomson. "Two Rapid Methods of Estimating Water in Crude Petroleum, Oil Fuel, and similar Substances," by H. S. Shrewsbury. "Note on Vinegar," by J. S. Jamieson.

THURSDAY, 5th.—Chemical, 8.30. "Mechanism of the Action of Fused Alkalis—Part I., Action of Fused Potassium Hydroxide on Dihydroxystearic Acid and Dihydroxybenzoic Acid," by H. R. Le Sueur and J. C. Withers. "Studies in the Succinic Acid Series—Part II., Anilides and Anilic Acids, and the Effect of Stearic Hindrance on the Formation of the Amides," by G. F. Morrell. "Some Homologues of Alizarin," by H. Bradbury and C. Weizmann. "Rotatory Powers, Refractivities, and Molecular Solution Volumes of Cinchotoxine and some Derivatives," by D. H. Peacock. "The Reaction between Benzylamine and the Dibromosuccinic Acids," by E. P. Frankland. "Isomeric Transformation of Ammonium Methylsulphate and of Substituted Ammonium Methylsulphates—The Interaction of Amines and Methylsulphates," by E. A. Werner.

Royal Society. "Luminous Vapours Distilled from the Air, with applications to the Study of Spectrum Series and their Origin" (II.), by Hon. R. J. Strutt. "Production of Neon and Helium by the Electrical Discharge," by J. N. Collie, H. S. Patterson, and I. Maeson. "Flow of Viscous Fluids through Smooth Circular Pipes," by C. H. Lees. "Quantitative Measurements of the Absorption of Light—I., The Molecular Extinctions of the Saturated Aliphatic Ketones," by F. O. Rice. "Ignition of Gases by Condenser Discharge Sparks," by W. M. Thornton. "Spark Spectrum of Nickel under Moderate Pressures," by E. G. Bilham.

THE CHEMICAL NEWS.

VOL. CX., No. 2867.

THE ABSORPTION OF LIGHT BY WATER CHANGED BY THE PRESENCE OF STRONGLY HYDRATED SALTS, AS MEASURED BY MEANS OF THE RADIO-MICROMETER. BEARING OF THE RESULTS ON THE SOLVATE THEORY OF SOLUTION.

By E. J. SHAEFFER, M. G. PAULUS, and HARRY C. JONES.

A PAPER bearing essentially the above title was published in *Diese Zeitschrift* (1913, xiv., 278) last year by Guy, Shaeffer, and Jones. It was therein recorded that aqueous solutions of salts which do not hydrate to any appreciable extent, the salts themselves having no absorption, are nearly as transparent as pure water. A layer of water, and a layer of the solution having a depth of water equal to the depth of the pure water, had essentially the same absorption. The slight differences could be accounted for as due to the slight hydration of the salts in question.

When strongly hydrated salts were used, however, very different results were obtained. The solutions were more transparent than pure water for certain wave-lengths, and the absorption bands were shifted towards the red. Since results of the above character were always obtained whenever a non-hydrating salt was used, and since the last-named results manifested themselves whenever a strongly hydrating salt was employed, we concluded that the phenomenon was closely connected with hydration. The simplest explanation seemed to be that "combined" water had a different absorption, and, indeed, less absorption than "free" water.

A paper has just appeared by A. K. Angström on the "Selective Reflections from Solutions in the Infra red" (*Physical Review*, 1914, iii., 47), which records results of the same general character as those found in this laboratory from the study of the absorption spectra of solutions. Angström found that solutions of salts which do not hydrate, or which hold their water of hydration loosely; such as sodium chloride, potassium nitrate, sodium and copper sulphates, do not shift the refraction maximum appreciably; while solutions of the strongly hydrated salts, calcium chloride and strontium chloride, shift both the maximum and minimum to about the same extent, showing a real change in the position of the band.

Improvements in the Apparatus.

The above results were so surprising and of such fundamental importance as bearing on the solvate theory of solution, that it was desirable to repeat the study of the salts earlier investigated and to supplement this with the investigation of other strongly hydrated compounds. Before this was done it was desirable to improve the apparatus at every possible point.

The radio-micrometer was provided with a more stable support. It was surrounded on all sides with a layer of cotton about one foot thick, only the junction being exposed to the radiation. The instrument showed no disturbing drift, and when the room was kept at a reasonably uniform temperature the position of the zero was remarkably constant. The Nernst glower used as the source of light was inclosed in a box of asbestos wool, which efficiently protected the glower from air currents. That the intensity of the current was kept very constant was shown by the close agreement of the duplicate readings given in the tables.

The cells used for holding the solutions were the same in principle as those employed in the earlier work; the

method for adjusting the distance between the ends was, however, greatly improved. A nut was carefully constructed and screwed on to the outer part of the cell in such a manner that the inner portion was raised or lowered according to the direction in which the nut was turned. Each complete revolution of the nut increased or decreased the distance between the plates by 1 mm. The nut was divided by means of the dividing engine into 100 divisions. By means of this arrangement we experienced no difficulty in setting the plates at a desired distance apart, to within less than one-hundredth of a mm. The cells used were made as nearly alike as possible, the glass ends being set parallel to one another. How nearly this result was attained is shown by the following data, which give the actual deflections when 10 mm. of water were used in each cell. The drum-head of the spectroscope was set at intervals of ten over the entire region of the spectrum which was studied, and whenever it became necessary to re-set the plates in either cell, this cell was tested against the other, to insure that under the same conditions both cells gave the same deflections.

The following table will show the degree of concordance of the results obtained with the two cells:—

λ .	Cell I.	Cell II.
706	27.5	27.5
746	38.0	38.0
787	50.5	50.5
833	65.0	65.0
886	79.5	79.0
941	91.5	92.0
1003	79.5	79.5
1006	123.0	123.0
1138	135.5	136.0
1216	63.5	63.5
1292	65.0	65.0
1362	45.5	45.5
1429	7.0	7.0

The experimental problem was to measure the transmission of a given layer of the solution, and then to compare this with the transmission of a layer of pure water containing just as much water as was present in the solution. To study the 1 μ water-band we selected 20 mm. of the solution, while 10 mm. were taken to study the 1.25 μ water-band. These depths of the solution did not give for any wave length a deflection upon the scale that was less than 25 mm. The maximum deflection obtained under these conditions was about 230 mm. It was only at the beginning of the first water-band, and at the very end of the first and second water-bands, that these depths of the solution gave deflections as small as 25 mm. Under ordinary conditions we could read the scale to one-half a mm.

A differential method was employed in determining the transmission of a given layer of solution and of solvent. Suppose the solution contained 80 per cent by volume of water. One cell was so set that the depth of the solution in it was 21 mm. The depth of the solution in the second cell was 1 mm. The deflection given by the deeper layer, divided by that given by the more shallow layer, gave the absolute transmission of a layer of the solution which was 20 mm. deep. From the above assumption there was 16.8 mm. of water in the one cell and 0.8 of a mm. of water in the second cell. The cells were then filled with these depths of water, and the transmission of 16 mm. of water obtained by the above named differential method. This method, then, compares under the same conditions the transmission of the water in the solution with that of the same depth of pure water. The percentage of water was obtained from the specific gravity and the concentration of the solution.

In the following tables it is to be noted that for the wave-lengths λ 706, λ 1003, and λ 1246 duplicate results are given. Both water and solution have about 97 per cent transmission at λ 706, and after placing the cells in

position a large number of readings were taken to get the actual transmission at this point. After ten or fifteen subsequent readings had been made wave-length λ 706 was again thrown on the junction to see if any change had occurred. Usually, no appreciable change was noted. This procedure was repeated for λ 1003 and λ 1246 after the entire series of readings had been completed.

In calibrating the head of the prism, certain water-bands were used in the infra-red. By making duplicate readings at λ 1003 and λ 1246 we could assure ourselves that the position of the prism had not shifted.

In the following tables the wave-lengths are given under λ . The transmissions of the salts used and their concentrations are given in the columns under the salts in question. The transmissions of water, which are comparable with those of the salt in question, are given in the same horizontal line and next to the salt.

Attention is called to the two series of measurements for magnesium chloride in Table I. The work for the second series was done four weeks after that for the first series, using the same solution in each case. Considering this fact and the inherent difficulties involved, we regard the agreement between the two series of results as fairly satisfactory. Wherever the 1μ water-band was studied

TABLE I.—Depth of Cell 20 mm.

λ .	KCl, 3.5 N.	H ₂ O.	MgCl ₂ , 4.49 N.	H ₂ O.	MgCl ₂ , 4.49 N.	H ₂ O.
706	98.4	98.0	96.4	97.3	96.4	96.4
706	98.4	98.0	95.3	97.3	97.3	97.3
746	93.6	96.0	90.3	94.9	93.7	93.7
766	92.5	94.5	93.7	95.4	92.3	94.6
770	—	—	92.8	94.8	91.6	95.1
774	—	—	92.0	95.7	92.8	93.9
778	—	—	90.3	94.3	91.2	93.1
787	93.5	94.3	92.0	96.2	94.4	95.3
809	96.5	96.5	92.2	95.8	92.7	95.1
833	93.3	94.0	93.0	94.0	93.6	93.5
857	90.7	92.1	88.9	91.8	91.2	91.6
886	90.0	90.5	88.5	90.4	90.4	89.9
913	89.8	88.5	85.3	88.7	87.3	88.3
941	81.5	81.3	80.6	79.7	82.3	79.7
952	72.7	72.3	74.6	70.0	76.7	71.4
965	63.1	61.1	65.6	59.0	67.4	60.8
972	56.8	56.3	60.7	54.4	61.7	54.7
978	51.8	51.3	56.2	49.7	56.6	50.8
984	48.5	47.8	52.7	46.6	53.3	47.3
990	45.2	45.2	49.4	45.1	49.6	45.3
996	44.3	45.0	46.8	44.7	47.0	44.6
1003	43.8	44.6	46.0	44.9	46.0	45.5
1003	43.8	45.0	47.2	45.3	46.3	45.3
1010	45.8	45.8	45.6	46.8	46.0	46.5
1017	46.7	47.5	46.7	48.3	46.8	48.4
1024	50.0	50.0	48.7	51.3	48.6	50.3
1029	52.6	52.5	50.7	53.7	49.9	52.9
1035	55.9	55.2	53.3	57.0	52.8	55.3
1041	59.2	58.7	56.2	60.0	55.5	58.4
1053	66.2	64.8	62.2	66.3	61.6	64.3
1066	71.8	70.3	66.7	71.5	65.3	68.7
1081	75.3	73.2	70.9	74.3	68.7	73.3
1195	76.5	74.8	71.5	75.7	71.2	74.3
1110	75.3	74.3	70.4	74.2	74.4	73.4
1123	73.0	71.5	67.3	70.2	64.4	71.2
1138	66.7	65.8	63.3	64.1	63.4	64.8
1146	62.4	61.0	—	—	—	—
1153	57.3	56.0	56.6	53.7	57.7	55.2
1161	52.1	49.6	51.6	47.4	52.8	50.0
1168	45.8	44.7	46.8	41.7	48.6	43.0
1175	39.5	38.3	41.5	34.8	43.7	37.0
1183	33.8	32.5	36.2	29.5	37.3	31.8
1192	28.5	27.2	30.4	24.5	32.2	26.4
1200	22.8	21.9	26.1	19.6	27.4	21.6
1208	18.2	17.1	21.3	16.1	23.2	17.4
1216	14.5	14.7	17.8	14.2	19.1	14.5
1224	12.7	12.7	14.8	12.6	15.7	12.6
1231	12.1	12.1	13.4	11.8	13.5	11.8

TABLE II.—Depth of Cell 10 mm.

λ .	KCl, 3.5 N.	H ₂ O.	KCl, 3.5 N.	H ₂ O.	MgCl ₂ , 4.49 N.	H ₂ O.
706	97.0	99.0	98.3	98.3	98.3	96.5
706	97.0	99.0	98.3	98.3	98.1	96.5
1153	72.9	73.6	73.3	73.5	74.8	72.7
1168	63.2	63.4	63.1	63.4	67.2	62.3
1175	58.2	58.3	58.2	58.3	62.6	57.4
1183	52.5	53.6	52.0	53.5	58.5	52.9
1192	47.8	48.5	47.0	48.5	55.1	48.7
1200	42.7	44.4	42.4	44.5	49.7	44.3
1208	38.3	40.2	37.7	40.0	45.8	40.0
1216	34.8	37.2	34.0	37.4	41.7	37.0
1231	33.0	34.5	31.6	34.6	36.9	34.0
1238	31.6	33.2	31.0	34.2	35.5	33.8
1246	31.0	33.2	31.4	34.1	34.2	33.3
1246	31.2	33.5	31.6	34.0	34.2	33.3
1254	—	—	—	—	33.6	33.8
1261	32.7	33.3	33.0	34.2	33.4	34.3
1269	33.4	34.4	33.4	35.4	33.8	34.6
1278	34.6	34.6	34.8	34.3	34.9	35.4
1292	36.1	35.1	36.6	35.4	35.0	35.7
1306	37.0	35.1	37.6	35.2	35.1	35.4
1313	37.2	34.7	38.0	35.1	35.6	35.2
1321	36.9	33.4	37.3	33.8	34.3	34.3
1334	35.7	32.3	35.0	32.3	33.0	32.2
1348	32.8	29.1	31.7	28.9	31.0	28.8
1362	28.7	24.4	27.5	24.2	28.2	24.5
1377	24.2	19.7	24.5	20.2	23.6	20.4
1388	19.0	15.8	18.0	15.8	19.5	15.4
1400	15.1	12.5	14.0	12.2	15.5	11.9
1414	11.3	10.0	10.0	9.5	14.1	11.7

the depth of solution used was 20 mm. The depth of solution was 10 mm. when the 1.25μ water-band was studied. It should be noted that two series of measurements are given for potassium chloride. The agreement is satisfactory, and shows that essentially the same results can be obtained when the work is repeated. When the work was duplicated with potassium chloride a new solution was prepared. In a number of cases the readings for individual wave-lengths were repeated.

Most of the tables of data have been omitted to save space, these being incorporated in the curves. In Table I. duplicate results are given for magnesium chloride, while in Table II. duplicate results are given for potassium chloride. These will show the degree of concordance between successive readings, and give some clue to the reliability of the results.

(To be continued).

A FURTHER STUDY OF THE PREPARATION AND PROPERTIES OF THE AMMONIUM SALTS OF ORGANIC ACIDS.

By LE ROY McMASTER.

IN continuation of the investigation of the preparation and properties of the neutral ammonium salts of organic acids, I still find that the salts were always prepared by neutralising an aqueous solution of the organic acid with ammonia water or ammonium carbonate, and the solution allowed to evaporate. As a result, the acid salts, instead of the neutral salts, were generally obtained, due to the hydrolytic action of water upon them. The properties given are thus the properties of the acid salts. In some cases no record at all can be found of the preparation of any ammonium salt of the organic acid. Many of the salts also contained water of crystallisation.

(For previous papers on this subject see *Am. Chem. Journ.*, 1913, xlix., 84, 294; *Journ. Am. Chem. Soc.*, 1914, xxxvi., 742; *CHEMICAL NEWS*, 1913, cviii., 136, 182, 193; 1914, cx., 212).

In attempting to prepare some neutral di-ammonium salts by the above general method, Keiser and McMaster always obtained the acid salts (*Am. Chem. Journ.*, 1913, xlix., 84). They then dissolved the organic acids in absolute ethyl alcohol or ether, and conducted a stream of dry ammonia gas into the solution. By this method they were thus able to prepare neutral di-ammonium salts of several of the organic acids. I (*loc. cit.*) continued the preparation of neutral ammonium salts in methyl alcohol, ethyl alcohol, and ether, and studied their properties, many of which were found to be different from those described in the literature. There have been prepared by this method, in the chemical laboratory of Washington University, the neutral ammonium salts of propionic, butyric, isobutyric, isovaleric, caproic, malonic, succinic, glutaric, ethyl malonic, adipic, pimelic, sebacic, fumaric, maleic, itaconic, citraconic, mesaconic, tartronic, malic, tartaric, racemic, crotonic, benzoic, cinnamic, *o*-phthalic, and *m*-phthalic acids.

The work on the preparation of neutral ammonium salts of organic acids and a study of their properties has been continued. There have been prepared and studied the neutral ammonium salts of palmitic, stearic, oleic, elaidic, aconitic, salicylic, *m*-hydroxy benzoic, *p*-hydroxyacetic, *p*-methoxybenzoic, hydrocinnamic, hippuric, *o*-toluic, phenyl acetic, mandelic, and uvicic acids. They were prepared in absolute alcohol and ether. Several were prepared also in acetone.

Some of the ammonium salts of the organic acids are more or less soluble in alcohol, and, when such was found to be the case, they were generally precipitated from a saturated solution. Before filtering, ether was generally added to decrease their solubility. As a rule, the salts were generally precipitated in a crystalline form from the alcoholic solution and in an amorphous condition from the ethereal solution. On passing ammonia into the solutions, there are frequently formed at first gelatinous or mucilaginous precipitates which generally change in a short time to crystalline or amorphous powders. This happens more frequently in the ethereal solution than in the alcoholic. In the acetone solutions so far studied, granular powders are formed at once on passing in the ammonia.

In the following work the neutral ammonium salts of palmitic, stearic, oleic, and elaidic acids were prepared and analysed by Mr. John D. Fleming, jun. The ammonium salicylate and hippurate were also analysed by Mr. Fleming, to whom I desire to express my sincere thanks.

Of the Higher Fatty Acids.

Ammonium Palmitate.—On attempting to prepare the neutral ammonium salt of palmitic acid by treating the acid with ammonia, Fremy obtained the acid salt, insoluble in cold water (*Ann.*, 1840, xxxvi., 46). The neutral salt can be readily prepared by passing dry ammonia gas into an ethereal solution of the acid, when it is formed as a very voluminous white gelatinous precipitate. It does not become crystalline even after passing in the gas for three hours. This precipitate was first filtered by suction, washed with ether, and dried in the air. Prepared in this manner, it lost ammonia and turned to a yellow curdy substance resembling a "soap." The freshly precipitated substance was next quickly filtered by suction on an alundum crucible, placed in a glass tube, and a current of dry ammonia conducted over it to remove the ether. It was then placed for a few minutes in a vacuum desiccator and analysed. Determination of the nitrogen by the Kjeldahl method proved it to have the composition of the neutral salt.

Calculated for $C_{16}H_{31}O_2(NH_4)$, 5.13 per cent; found, 5.16 per cent N.

The neutral salt when first precipitated is white, but soon becomes somewhat yellow. It is not hygroscopic, but loses ammonia, especially in moist air. It is slightly soluble in ether and petroleum ether, readily soluble in

methyl alcohol, ethyl alcohol, and acetone, and insoluble in carbon tetrachloride and benzene. There is a considerable frothing when the salt is shaken with water.

Palmitic acid was also dissolved in ethyl alcohol, and the solution treated with ammonia gas. After a short time a crystalline precipitate was formed which went into solution upon the addition of a small amount of alcohol. The solution was poured into a crystallising dish and the alcohol allowed to evaporate. The salt obtained was at first pure white, but before the evaporation was complete it became yellowish. After the alcohol had entirely evaporated and the salt became dry it had the appearance of the compound prepared in ether. It had lost ammonia, and analysis proved it to be the acid salt. In order to obtain neutral ammonium palmitate it was thus very evident that the salt must not be exposed to the air for any length of time. The compound prepared in either alcohol or ether is evidently an ammonium "soap."

Ammonium Stearate.—Stearic acid was dissolved in ether and dry ammonia conducted into the solution. A white gelatinous precipitate was formed, which, after a short time, appeared to be somewhat crystalline. Like the palmitate this salt loses ammonia in ordinary air, and it was necessary to filter it very quickly by suction and dry it in a current of ammonia gas. The salt thus prepared is not hygroscopic, is stable in dry air, but loses ammonia in moist air. It is practically insoluble in ether, benzene, carbon tetrachloride, and petroleum ether, but very soluble in methyl alcohol, ethyl alcohol, and acetone. It froths considerably when shaken with water. When an alcoholic solution of the acid is saturated with ammonia gas and the mixture allowed to evaporate in the air, there is obtained a soapy residue which analysis shows to be an acid salt instead of the neutral salt. This is due to the fact that it has lost ammonia during the evaporation of the alcohol. When a small amount of the neutral salt prepared in ether was dissolved in alcohol and the alcohol quickly evaporated, the residue was partly amorphous and partly made up of needle-like crystals. We have with the stearate another example of an ammonium soap.

Determinations of the nitrogen by the Kjeldahl method gave results slightly higher than the calculated amount for the neutral salt. This may have been caused by a small amount of free ammonia not being removed, although the salt was placed over sulphuric acid in a vacuum desiccator.

Calculated for $C_{18}H_{35}O_2(NH_4)$, 4.65 per cent; found, 4.80 and 4.81 per cent N.

Ammonium Oleate.—For the preparation of liquid crystalline ammonium oleate, Lehmann has made the neutral anhydrous ammonium oleate by passing ammonia gas from a steel cylinder into oleic acid until it smells strongly of ammonia (*Sitz. b. Heidelberger Akad. Wiss.*, 1913, A, xiii. *CHEMICAL NEWS*, 1913, cviii., 191). If this preparation is fused under a cover-glass on a slide, and "the cooling is watched under a microscope, it is seen that the mass solidifies as a whole to small needle shaped (rhombic?) crystals of a labile modification. These are soon converted into a rather less fusible stable modification appearing as imperfectly formed (monoclinic?) leaflets. From alcoholic solution these latter can be obtained as relatively large crystals with sharp edges." Lehmann also states that an anhydrous acid ammonium oleate does not exist and that solid neutral ammonium oleate dissolves in oleic acid, from which it crystallises out again unchanged. The neutral anhydrous ammonium oleate can also be prepared by conducting dry ammonia gas into an ethereal solution of oleic acid. At first there is formed a white gelatinous precipitate which becomes somewhat crystalline after running in the gas about one hour. It is impossible to filter the mixture even by suction. The ether was removed by a current of dry ammonia gas and the salt finally dried in a stream of dry air. It is very deliquescent and loses ammonia easily in moist air. When shaken with water it forms a milky suspension.

Calculated for $C_{18}H_{33}O_2(NH_4)$, 4.68 per cent; found, 4.67 per cent N.

When it was found that the ether could not be removed by filtration from the precipitated salt the mixture was poured into a crystallising dish. When the ether had evaporated there remained a very viscous liquid which, on stirring, became semi-solid. During the evaporation of the ether moisture was taken up by the gelatinous precipitate, and there was presumably formed neutral ammonium oleate hydrate. This is practically what was observed by Lehmann (*loc. cit.*) in the preparation of liquid crystalline ammonium oleate:—"If we continue to add water to the solid anhydrous crystals of ammonium oleate it may easily be seen under the microscope that when the amount of water has reached a certain definite limit, the whole mass is converted into the syrupy liquid crystalline modification. Thenceforward no needles or leaflets of the anhydrous modification appear; the mass has become neutral ammonium oleate hydrate." That the mass referred to above will take up moisture readily was also noted by Lehmann for—"it is sufficient to leave the preparation uncovered for some time, when it absorbs moisture from the air, or to breathe on it."

Ammonium Elaidate.—No record can be found of the preparation of this salt. Elaidic acid was dissolved in ether, and ammonia passed into the solution. A glistening white gelatinous precipitate was formed, which was filtered, washed with ether, and dried in a current of dry air. When thus dried it became an amorphous soap-like substance. Ammonium elaidate can also be prepared in alcohol by saturating an alcoholic solution of the acid with ammonia gas, and allowing the alcohol to evaporate. Since this salt loses ammonia slowly in the air, it is better to pass the ammonia gas into a saturated alcoholic solution of the acid when white translucent crystals are precipitated at once. These can be filtered, washed with ether, and dried in a desiccator. White crystalline flakes are thus formed. The salt prepared in either medium is not deliquescent. The salt is soluble in methyl alcohol, ethyl alcohol, acetic acid, and acetone. Analysis of the salt prepared in ether showed it to be neutral ammonium elaidate.

Calculated for $C_{18}H_{33}O_2(NH_4)$, 4.68 per cent; found, 4.61 per cent N.

Of a Tribasic Acid.

All the previous preparations have been the neutral salts of monobasic and dibasic acids. The method having proved so very applicable in these cases it was tried on the preparation of a neutral ammonium salt of a tribasic acid. Neutral ammonium aconitate was prepared, but only with difficulty, on account of it being so very deliquescent and losing part of its ammonia so readily. It suffices to show that the method is of very general application.

Ammonium Aconitate.—Several attempts were made to prepare the neutral ammonium salt of aconitic acid. When ammonia is passed into a solution of the acid in ether or in methyl alcohol a mucilaginous precipitate is formed. This will not crystallise even if the ammonia is conducted into the ethereal or alcoholic solution for a long time. A white colloidal precipitate is formed if the ammonia is passed into a solution of the acid in ethyl alcohol. After standing four days this precipitate settled out mostly as an amorphous powder, but a small part of it was gummy. It was not analysed. Baup has also found that the neutral ammonium salt of aconitic acid will not crystallise (*Ann.*, 1851, lxxvii., 302). The salt was prepared by Baup in aqueous solution and allowing the solution to evaporate to crystallisation.

Ammonia was then passed into a saturated alcoholic solution of the acid to which a small amount of ether was added. A granular precipitate was now formed. This was quickly filtered by suction, washed with ether, and placed over sulphuric acid in a vacuum desiccator for a short

time. Analysis of two samples of the salt thus prepared gave, respectively, 16.08 per cent and 16.09 per cent of nitrogen. The neutral salt of aconitic acid contains 18.67 per cent nitrogen. Since this salt is very deliquescent and readily loses ammonia, it was again prepared as just described, and placed in a desiccator containing sodium hydroxide instead of sulphuric acid. Two analyses of this salt gave, respectively, 18.63 per cent and 18.65 per cent nitrogen, showing that it was the neutral compound. This salt gave a neutral solution when dissolved in water, in which it is very soluble, but soon hydrolyses. It is soluble in acetic acid, slightly soluble in methyl and ethyl alcohols, and insoluble in ether.

Of the Hydroxy-benzoic Acids.

Ammonium Salicylate.—Cahours prepared the normal salt of salicylic acid by evaporating a hot concentrated solution of salicylic acid and ammonia water (*Ann.*, 1844, lii., 336). Upon cooling, the ammonium salt crystallised out in scales. A dilute solution produced by slow evaporation glittering silky crystals, which dried in the air had the composition $NH_4C_7H_5O_3$. The salt was found to be very soluble in water; by dry distillation, it decomposed into water and the amide of salicylic acid. Marignac obtained this salt as monoclinic crystals containing 0.5 molecule of water of crystallisation (*Fahresb. Fortschritte Chem.*, 1855, p. 485).

When ammonia gas was passed into an ethereal solution of salicylic acid white pearly scales were formed. An aqueous solution of the salt was neutral, and produced, with ferric chloride, a wine-red colour. It is not deliquescent, and loses ammonia only in moist air. It is very soluble in water, methyl alcohol, ethyl alcohol, and acetic acid.

Calculated for $C_7H_5O_3(NH_4)$, 9.03 per cent; found, 9.04 per cent N.

Ammonium-m-hydroxybenzoate.—The ammonium salt of m-hydroxybenzoic acid was first prepared by Barth by dissolving the acid in dilute ammonia water and allowing the solution to evaporate (*Ann.*, 1868, cxlviii., 36). The salt crystallised in needles in fascicular aggregates, and was found to be very soluble in water. It contained no water of crystallisation, and lost ammonia if dried on the water-bath. Analysis of the air dried salt showed it to have the formula $C_7H_5O_3NH_4$.

When ammonia gas is passed into an ethereal solution of m-hydroxybenzoic acid until a portion of the salt, on being dissolved in water, shows a neutral solution, there is formed a white granular precipitate of neutral ammonium-m-hydroxybenzoate. When the ammonia is first passed in, the precipitate formed is very mucilaginous. The salt was washed with ether, and dried in a vacuum desiccator. It is not deliquescent. In dry air the salt is stable, but loses ammonia in moist air. It is soluble in methyl alcohol, ethyl alcohol, and acetic acid. It gives no colour with ferric chloride. The salt crystallises from ethyl alcohol in needles.

This salt can also be precipitated in acetone, in which it is but slightly soluble. When the ammonia is passed into the solution of the acid in acetone, no mucilaginous precipitate is formed at first, as in the case of the ethereal solution, but a granular powder is formed at once. The salt prepared in either acetone or ether slowly hydrolyses when dissolved in water.

Prepared in ether—Calculated for $C_7H_5O_3(NH_4)$, 9.03 per cent; found, 9.05 per cent N.

Prepared in acetone—Found, 9.02 per cent N.

Ammonium p-Hydroxybenzoate.—This salt has been prepared by neutralising the aqueous solution of p-hydroxybenzoic acid with ammonia water, and the solution allowed to evaporate. It crystallised out from solution in long prisms, and contained one molecule of water of crystallisation.

This salt can also be prepared by passing dry ammonia

gas into a saturated alcoholic, an ethereal, or an acetone solution of the anhydrous acid. In the alcoholic solution fine needle-like crystals are formed, in the ethereal solution a gelatinous precipitate is first formed which turns to an amorphous powder, while an amorphous powder is formed at once in the acetone solution. The salt was filtered by suction and washed with ether in each case. It is not deliquescent, and imparts a neutral reaction to water in which it is very soluble. It slowly hydrolyses when dissolved in water. The aqueous solution gives no colour with ferric chloride. It loses ammonia in moist air. The salt is readily soluble in methyl alcohol and acetic acid, very slightly soluble in acetone, and appreciably so in ethyl alcohol. It is insoluble in ether. Analysis was made of the salt prepared in ether.

Calculated for $C_7H_5O_3(NH_4)$, 9.03 per cent; found, 9.05 per cent N.

Ammonium p-Methoxybenzoate.—The ammonium salt of *p*-methoxybenzoic acid (anisic acid) is described by Laurent to be rhombic plates of the composition $NH_4C_8H_7O_3$ (*Berz. Jahrb.*, xxiii., 415). When ammonia was passed into a solution of the acid in alcohol, pearly white crystalline leaflets were formed, which were filtered, washed with ether, and dried in a vacuum desiccator. The salt is stable in the air, and an aqueous solution of it is neutral to sensitive litmus-paper. It is not deliquescent, and its aqueous solution does not hydrolyse. It is readily soluble in methyl alcohol and acetic acid, and appreciably so in ethyl alcohol and acetone. A white curdy precipitate, soluble in ammonia water, is formed when silver nitrate is added to an aqueous solution of the salt.

Calculated for $C_8H_7O_3(NH_4)$, 8.29 per cent; found, 8.31 per cent N.

When ammonia gas was conducted into an ethereal solution of *p*-methoxybenzoic acid there was first formed a gelatinous precipitate which changed to a fine crystalline powder. It can be crystallised from acetone in the form of fine feather-like needles.

Of some other Aromatic Acids.

Ammonium Hydrocinnamate.—Beilstein describes this salt as small leaflets, easily soluble in water and readily losing ammonia (see Gjacosia, Hoppe-Seyler's, *Zeit. Phys. Chem.*, 1883, viii., 109). When ammonia is run into an ethereal solution of hydrocinnamic acid there is formed a white gelatinous precipitate, which on drying changes to white lustrous leaflets. The salt thus formed is the neutral ammonium hydrocinnamate, soluble in water, methyl alcohol, ethyl alcohol, and acetic acid. It is insoluble in ether. The salt is slightly hygroscopic, and loses ammonia in the air. Ferric chloride forms a yellowish precipitate with an aqueous solution of it.

Calculated for $C_9H_9O_2(NH_4)$, 8.38 per cent; found, 8.37 per cent N.

On account of the great solubility of this salt in ethyl alcohol it cannot be precipitated in this medium. Ammonia was run into a solution of 2 grms. of the acid in ethyl alcohol for one hour, the alcoholic solution poured into a crystallising dish, and allowed to evaporate in the air over night. A heavy oily substance remained instead of the pure salt. This oil was acid to litmus-paper. On distilling it ammonia was first evolved, then fumes which condensed to a white solid. The mercury of the thermometer then rose to 260° , and a heavy refractive oil passed over which re distilled at 245° (uncorr.). Hydrocinnamic acid is easily changed partly into its ethyl ester of boiling-point 247° (corr.) by merely dissolving it in ethyl alcohol (Erlenmeyer, *Ann.*, 1866, cxxxvii., 330). On the other hand, the ester just as readily changes back to the acid by the moisture of the air. Ethyl hydrocinnamate is also very refractive. The oily residue which was obtained above by allowing the alcoholic ammonia solution of hydrocinnamic acid to evaporate in the air was thus a mixture of hydrocinnamic acid, its ammonium salt, and its ethyl ester.

Ammonium Hippurate.—A salt of the formula $NH_4C_9H_8NO_3 \cdot C_9H_9NO_3 + H_2O$ was obtained by Schwarz by treating hippuric acid with an excess of ammonia (*Ann.*, 1845, liv., 37). He was unable to prepare the neutral salt, and no record of its preparation can be found. When ammonia gas was run into a saturated alcoholic solution of hippuric acid to which was added a small amount of ether, glistening pearly white laminae were formed. These were filtered on an alundum crucible, and washed with ether. The salt is stable in dry air, but loses ammonia slowly in moist air. It is not deliquescent, and an aqueous solution of it is neutral. It is soluble in methyl alcohol and ethyl alcohol. It is somewhat soluble in acetone, from which it crystallises in beautiful needles. It is insoluble in ether.

Determination of the total nitrogen by the Kjeldahl method proved it to have the composition of the neutral salt.

Calculated for $C_9H_8NO_3(NH_4)$, 14.29 per cent; found, 14.30 per cent N.

Ammonium o-Toluate.—This salt cannot be precipitated by passing ammonia into an alcoholic solution of the acid on account of its great solubility in the alcohol. When the solution is evaporated, crystalline needles are formed. A fine white crystalline precipitate is formed if the gas is passed into an ethereal solution of the acid. The salt is not deliquescent but is readily soluble in water, giving a neutral solution. The salt is stable in dry air, but loses ammonia slowly in moist air. It is soluble in methyl alcohol, ethyl alcohol, acetic acid, and acetone.

Calculated for $C_8H_7O_2(NH_4)$, 9.15 per cent; found, 9.15 per cent N.

Although some of the salts of *o* toluic acid have been prepared and studied, no mention of the neutral ammonium salt can be found.

Ammonium Phenylacetate.—This salt was prepared by Moller and Strecker by dissolving the acid in ammonia water, and allowing the solution to evaporate to crystallisation (*Ann.*, 1860, cxiii., 66). The salt was obtained only with difficulty on account of its great solubility. Fine white needles are formed if ammonia gas is conducted into a saturated alcoholic solution of phenyl acetic acid, while a fine white semi-crystalline precipitate is formed if the ammonia is run into an ethereal solution of the acid. Before filtering off the crystals formed in the alcoholic solution it is necessary to add ether, for they are quite soluble in the alcohol. The salt is fairly stable in the air, losing its ammonia but slowly in moist air. The salt does not deliquesce, and imparts a neutral reaction to a water solution of it. It is very soluble in water, methyl alcohol, and acetic acid, but only slightly so in acetone.

Prepared in alcohol—Calculated for $C_8H_7O_2(NH_4)$, 9.15 per cent; found, 9.12 per cent N.

Prepared in ether—Found, 9.15 per cent N.

Ammonium Mandelate.—This salt was first prepared by Winckler by treating an aqueous solution of mandelic acid with ammonia water, and allowing the solution to evaporate slowly (*Ann.*, 1836, xviii., 317). The ammonium salt crystallised out only with difficulty as a yellowish white soft mass, extremely soluble in water and alcohol. Duparc and Pearce prepared the salt in the form of rhombic prisms (*Zeit. Kryst. Min.*, xxvii., 611).

The neutral ammonium salt of mandelic acid was prepared by the usual method in ether. When the ammonia was added there was first formed a white mucilaginous precipitate which soon changed to a fine crystalline powder, very soluble in water, methyl alcohol, ethyl alcohol, and acetic acid, but insoluble in ether and acetone. The salt, being very deliquescent in the air, was quickly filtered, washed with ether, and dried for a short time over sulphuric acid in a vacuum desiccator. It gave a neutral solution when dissolved in water. It loses ammonia in moist air. The salt can be crystallised from ethyl alcohol in aggregates of fine needles.

Calculated for $C_8H_7O_3(NH_4)$, 8.28 per cent; found 8.29 per cent N.

Ammonium Uvitate.—No record can be found of the preparation and properties of this salt other than being mentioned by Finck that it is impossible to precipitate it out of its aqueous solution by alcohol (*Ann.*, 1862, cxxii., 186). When dry ammonia gas was run into an alcoholic solution of uvitic acid no precipitate was formed. Upon the addition of ether to this solution a white flocculent precipitate was formed. This was filtered by suction, keeping the alundum crucible filled with ether to prevent the salt going into solution on account of the alcohol present. The salt dried in a vacuum desiccator to an amorphous powder. It is readily soluble in water, to which it imparts a neutral reaction. It is soluble in methyl alcohol, ethyl alcohol, and acetic acid, slightly soluble in acetone, and insoluble in ether. The salt is not deliquescent. The salt prepared in ether had these same properties, and analysis showed it to be the neutral ammonium salt of uvitic acid.

Calculated for $C_9H_6O_4(NH_4)_2$, 13.08 per cent; found, 13.10 per cent N.

This investigation is being continued with other organic acids, especially the substituted acid.—*Journal of the American Chemical Society*, xxxvi., No. 9.

THE RADIUM : URANIUM RATIO IN CARNOTITES.*

By S. C. LIND and C. F. WHITEMORE.

(Continued from p. 219).

IV. The Emanating Power of Carnotite.

The term "emanating power" was first used by Boltwood (*loc. cit.*) to signify the percentage loss of emanation from a radio-active ore, and was applied by him in the determination of radium as an additive correction to the quantity of emanation liberated by direct solution. The emanating power for many samples of carnotite has been found surprisingly large in the present investigation (compare Table IV., col. 6) varying from 16 to 50 per cent. This high degree of emanating power is not only to be noted as one of the distinguishing characteristics of carnotite, but has also formed such a controlling factor in the experimental procedure that it deserves some preliminary attention.

The loss of emanation by the ore is due to a diffusion of the gas and is much lower (only 3 to 8 per cent) in the case of dense, compact minerals like pitchblende than for carnotites which have a looser mechanical structure. For a given sample it is doubtless, as suggested by Rutherford, dependent on the degree of fineness of the ore ("Radio-active Substances and their Radiations," 1913, p. 64). We have not undertaken any direct investigation of the relation between emanating power and fineness, or any other property, but have ascertained that fineness cannot be the principal controlling factor among different specimens, as there is no relation whatever apparent between the order of fineness of different samples and their emanating power.

Evidently a given percentage error, in determining the emanating power to be used additively in obtaining the total emanation according to Boltwood, would more seriously influence the final result in case of a carnotite than in an ore where its relative value is small. Our earlier results showed on repetition considerable deviations in emanating power, which suggested that the emanation was not always removed to the same degree from the same sample. This is probably due to differences in the amount of air passed over the ore, or differences in air pressure or

velocity, resulting in drawing varying amounts of emanation out of a more or less porous structure. A simple remedy suggested itself as a modification of the Boltwood method, namely, to make the determinations of the emanating power and the emanation liberated by solution strictly complementary to each other, in the sense that each sample dissolved should represent part or the whole of the sample from which emanation had just been drawn to determine the emanating power. By this procedure it is indifferent whether various determinations of emanating power are concordant or not so long as the sums obtained by adding corresponding determinations are in agreement with each other. That the latter is in reality the case may be seen from Table I., in which it will be noted that, for each ore, the agreement for the total emanation is better than that of either of the individual values going to make up the sum. Only a few examples can be given in the table illustrative of this point, because it was soon found more convenient to determine the total emanation in one operation, as will be described below.

TABLE I.—Illustrating Advantage of "Complementary" Emanation Method.

Ore No. (a)	Eman. power in curies $\times 10^9$.	+ Soln. eman. in curies $\times 10^9$.	= Total eman. in curies $\times 10^9$ per 1 g. ore.
2.	15.0	87.1	102.1
"	17.6	84.5	102.1
4.	14.0	58.6	72.6
"	11.7	60.8	72.5
5.	21.8	27.7	49.5
"	23.6	26.2	49.8
8.	4.38	8.93	13.3
"	4.45	8.50	13.0

(a) This numbering of samples is the same as used throughout the paper. See Section VIII.

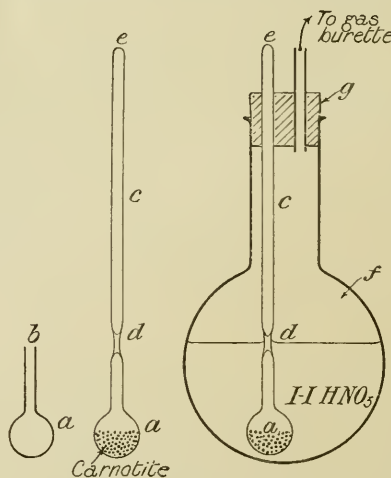


FIG. 1.—EMANATION METHOD, USING SEALED TUBE.

Unless one desires to know the emanating power itself, it is simpler to determine the total emanation in one operation by sealing the ore in a very thin bulb, of the type shown in Fig. 1, for a month or more before breaking under acid to liberate the total emanation.

This method checks excellently with the "complementary" modified Boltwood method, as will be seen from Table II. The bulb (a) of 4 to 10 mm. diameter, according to the quantity of ore to be used, is blown very thin so as to break without endangering the outer flask (f) containing HNO_3 . The weighed ore is introduced into the bulb through (b) and then the glass stem (c) is sealed

* Published by permission of the Director of the Bureau of Mines, U.S.A. From the *Journal of the American Chemical Society*, xxxvi., No. 10.

on and constricted to make a complete seal at (d) the upper end (e) being also sealed for convenience. The whole is introduced through a double-bored rubber stopper (g) just off the bottom of the flask (f) and may be broken by a slight downward rap on (e). By boiling the acid the ore is readily attacked, and all of the emanation is boiled over into a gas burette (compare Fig. 2). The good agreement between this method and the one already described may be seen from Table II.

TABLE II.—Comparing Results of "Sealed Bulb Method" (I) for Total Emanation in One Operation, with "Complementary Method" (II.).

Ore No.	Eman power in curies $\times 10^9$.	+	Soln. eman. in curies $\times 10^9$.	=	Total eman. in curies $\times 10^9$.
14.	I. —		—		11.09
	II. 3.906		7.188		11.09
15.	I. —		—		8.08
	II. 3.488		4.467		7.96
16.	I. —		—		7.08
	II. 3.191		3.916		7.11
18.	I. —		—		7.34
	II. 1.224		6.156		7.38
19.	I. —		—		8.54
	II. 2.993		5.606		8.60
20.	I. —		—		29.91
	II. 9.847		19.77		29.62
21.	I. —		—		23.61
	II. 10.72		13.12		23.84
22.	I. —		—		21.21
	II. 3.445		17.64		21.09

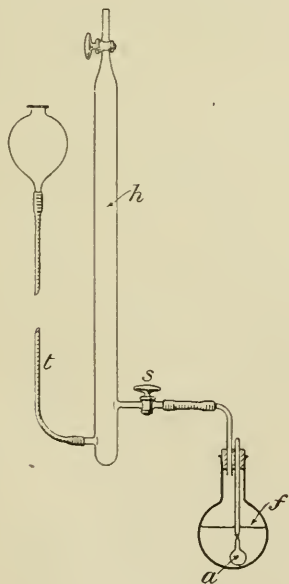


FIG. 2.—APPARATUS FOR DISSOLVING CARNOTITE AND COLLECTING THE EMANATION.

In connection with fusion methods to be later described, it was of interest to know the emanating power of the cold solidified mass resulting from the fusion of carnotite in sodium carbonate. On investigation its emanating power proved to be zero, which is in marked contrast with the action of carnotite in the cold without flux. Since we have always found (compare Table III.) great difficulty in removing emanation even out of the hot fusion of carnotite in $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ mixture, although the same method works well on pitchblende or crude sulphates, the following

suggested itself to us :—If the cold fusion loses no emanation, while the ore alone loses large percentages, it seemed plausible that a direct ignition of the ore with no flux might bring about the liberation of emanation more readily than with a flux. This procedure proved eminently successful with carnotite (though a complete failure for crude sulphates) and has served in all cases as a control for the solution method.

Impracticability of Solid Radiation Methods for Carnotite.—It should also be noted while dealing with emanating power that the high and variable values exhibited by carnotite seem to preclude the possibility of employing, for accurate determination, any radiation method from the solid ore for either alpha, beta, or gamma rays, unless, in the employment of the gamma-ray method, a large quantity of ore could be kept for a month and then measured in an absolutely tight vessel.

V. Emanation Method for the Determination of Radium.

For the liberation of emanation from carnotite we originally proposed to employ three methods: (1) Solution in boiling 1-HNO_3 (a) corrected for "emanating power" by the "complementary" method already described in Section IV.; (b) by a single operation, by dissolving ore in equilibrium with emanation from a sealed tube. By reference to Table II. it will be seen that both modifications of this method are equally suitable. (2) Fusion with a $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ mixture, which is later fused again in a Jena glass tube. This method will be seen from Table III. to give very low results for carnotite and was soon abandoned. Perhaps by means of electrical heating to a higher temperature the emanation could be expelled from the fusion. The heating employed, both here and for the direct ignition method, was by means of a Méker burner. A Jena glass tube, into which the ore or fusion is introduced directly (without boat) and held in place by glass-wool plugs, was held in the bare flame of this burner. (3) Direct ignition of the ore under conditions just described. This method was suggested by the high emanating power

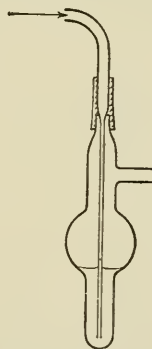


FIG. 2a.— H_2SO_4 MICRO-DRYING TUBE.

of carnotite and has proved entirely satisfactory, giving results which accord well with those of the solution method (cf. Table III.).

In the solution method the emanation always was allowed to stand in a gas burette for ten minutes before passing into the electroscopes, to allow any possible thorium emanation to decay; while in the ignition method air was passed directly over the heated ore through a small H_2SO_4 drying bulb into the exhausted electroscopes. The fact that both methods give concordant results indicates the absence of thorium in carnotite. This is further supported by the return of the natural leaks of the electroscopes after a few hours to their original values, which would not be the case for the induced activity of thorium. (4) Fusion with $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ followed by solution in 5 per cent Na_2CO_3 , filtration, solution of the residue in 1-3 HNO_3 , and subsequent boiling off of both alkaline and acid solu-

tions. This method, which is referred to as the *fusion and solution* method in Table III., will be seen to give results about 10–20 per cent low. This we attribute to the almost invariable precipitation of some colloidal silica, involving the adsorption of radium and consequent loss of some emanation.

Of the four methods tried, two were found suitable and two unsuitable, as will be seen from the comparative results in Table III.

TABLE III.—Comparative Results of Different Methods for De-emanating Carnotites.

Total emanation in curies $\times 10^9$ by method :				
Ore No.	(1) Solution in 1-HNO ₃ .	(2) Fusion with Na ₂ -K ₂ CO ₃ .	(3) Ignition.	(4) Fusion and solution.
2.	101.4	63.5	98.0	83.0
4.	72.6	—	73.3	53.8
13.	7.83	2.62	7.89	6.20
14.	11.09	—	11.63	8.92
15.	8.08	—	—	6.98
16.	7.11	—	7.17	—
17.	8.66	—	8.65	7.38

Solution and Boiling off the Emanation requires no especial explanation. The apparatus is shown in Fig. 2.

Hot water containing some NaOH is used in the gas burette (*h*); 1-HNO₃ is used as solvent in flask (*f*). A glass stopcock at (*s*) has been found more convenient than rubber tubing and a clamp. All possibility of loss of emanation by the passage of water into the side arm (*t*) is avoided by allowing all air to pass up into (*h*) before the bulb (*a*) is broken. In case of an ore not sealed in glass, the same may be accomplished by folding a filter-paper containing ore, so that it remains in the neck of flask (*f*) until all air is expelled and the steam softens the paper, allowing it to drop into the acid. The stopcock should be closed at this time, or on breaking the glass bulb, and then gradually opened to prevent a sudden rush of gas from carrying undissolved ore up into the alkali. Pitchblende used for standardisation purposes was treated in the same way as carnotite, either directly with correction for emanating power or from a glass tube which had been sealed one month.

For the ignition method the ore was sealed in a straight piece of Jena combustion tubing drawn down to capillary points at both ends. The tubes were about 4 to 10 mm. internal diameter, depending upon the volume of the sample, and about 15 to 20 cm. long. The weighed ore was introduced through one end, which was then drawn out and sealed. The ore is held in place in the middle portion of the tube by means of glass-wool plugs. After standing one month or more the tube was connected through H₂SO₄ micro-drying bulbs (*cf.* Fig. 2*a*) to the exhausted electroscope on one side and to the outside air on the other side. After breaking the capillary ends inside the rubber connections, air was allowed to sweep over the ore, the tube being heated by a Méker burner (1 1/16 inch grating) until the Jena glass completely collapsed. This treatment will be seen, by reference to Table III., to give complete de-emanation.

VI. The Electroscope Measurements.

Two electroscopes were employed, both of the Wilson type, with sulphur insulation between the leaf chamber and the ionisation chamber below. The volumes of the latter were about 1 and 1/2 litre, respectively, the former cubical and the latter cylindrical in shape.

Perhaps because of the symmetrical shape of the ionisation chambers it appeared to make little difference whether equilibrium with induced activity was attained with or without a charge on the instrument. Consequently, after allowing the gas to remain in the electroscope for three hours, a charge was put on for ten to fifteen minutes before taking a series of ten readings over 40 scale divisions. Quantities of emanation were usually intro-

duced such as to give a discharge of about 1 division per second.

Standardisation was carried out by dissolving about 40 mg. of carefully analysed (*cf.* Sections VIII. and XII.) pitchblende of Colorado in boiling 1-HNO₃, assuming the Ra/U ratio as 3.328×10^{-7} according to Heimann and Marckwald (*loc. cit.*). The analysis of pitchblende was carried out by the method employed for carnotite (*cf.* Section VII.), with the omission of the procedure for the separation of vanadium.

Data for Standard Pitchblende.—One grm. of standard pitchblende contains 0.765 grm. U₃O₈=0.649 grm. U= 2.16×10^{-7} grm. radium. Emanating power = 2.7 per cent. Therefore, 1 mg. dissolved directly gives 2.10×10^{-10} curies of radium emanation.

As a control of standardisation of the electroscopes, before each determination a gamma-ray measurement was carried out by placing a sealed glass tube, containing about 1 mg. of radium element in a tube fixed to the base of the discharge chamber, and measuring the rate of the discharge produced, which usually remained practically constant. Deviations of 2 to 3 per cent, attributable to variations in pressure and temperature of the air, were used as direct corrections instead of the usual barometric and temperature corrections. Deviations greater than 2 or 3 per cent were attributed to changes in the leaf system, necessitating recalibration. New calibrations were not found necessary oftener than in one to two months.

Emanation was introduced into the partially exhausted chamber through a micro-drying tube filled with H₂SO₄ (*cf.* Fig. 2*a*), any possible spray from which was prevented from entering the chamber by a short layer of cotton batting. After using the electroscope, the emanation was immediately removed by a current of dry air taken from outside the laboratory and the natural leak of the instrument determined the following day, before use.

VII. The Determination of Uranium.

The method which we have found most satisfactory for the determination of uranium in carnotite is a gravimetric one given below in full detail, including the volumetric determination of vanadium. Although having no direct bearing on the present subject we include in Section VIII. the data for vanadium in order to illustrate its occurrence in typical carnotites.

Gravimetric Method for Vanadium and Uranium in Carnotite and other Ores (*cf.* R. B. Moore and K. L. Kithil, *Bull.* lxx., p. 88, U.S. Bureau of Mines).—Treat from 2–5 grms. of ore, according to the amount of V, Fe, and U present, in a covered beaker, with 10 cc. HCl and let it stand fifteen minutes with occasional shaking. Add 5 cc. HNO₃ and heat on a steam bath. When quiet, remove the cover and evaporate to dryness. Add 3 cc. HCl and 5 cc. H₂O to the residue and let it stand on the steam bath for a few minutes, stirring occasionally. Dilute with 25 cc. hot water, filter into a small beaker, and wash the residue with warm water.

Some ores do not yield all the V to this treatment; a little of it may remain with the insoluble residue. To make sure that all V is in solution ignite the residue in a platinum dish, treat it with 5 cc. of HF and evaporate to dryness on a steam bath. Do not bake the residue. It is not necessary to expel all SiO₂. Add 3 cc. of HCl to the residue from the HF treatment, and evaporate to dryness. Repeat this treatment to insure expulsion of HF. Treat the residue with 2 cc. of HCl and 2 cc. H₂O and manipulate until any red crust is dissolved, dilute the solution with water and filter it into the main liquid.

Pass H₂S into the liquid to separate copper, &c., filter and boil the liquid to expel H₂S. Concentrate the liquid to 100 cc. if necessary, and oxidise it with an excess of H₂O₂ and then neutralise with dry Na₂CO₃, adding 2 or 3 grms. in excess. Boil the liquid for about fifteen minutes, until the yellowish U precipitate dissolves, leaving a brown precipitate which is principally iron. Filter and

wash the iron precipitate with water, reserving the filtrate. Dissolve the iron precipitate in the least possible amount of HNO_3 (1—1), and add 10 cc. of H_2O_2 , neutralise with Na_2CO_3 , add an excess of 2 grms. and boil as before. Filter into the beaker containing the first filtrate. The iron precipitate may contain a little V—reserve it for further treatment.

Concentrate the united filtrates from the iron precipitation to a volume of about 200 cc., add 10 cc. of strong HNO_3 and boil until all CO_2 is expelled. Neutralise the free acid with ammonia (until a slight permanent precipitate appears), then add 4 cc. of HNO_3 for each 100 cc. of liquid. Now add 10 cc. of a 20 per cent lead acetate solution, and enough (about 20 cc.) of a strong solution of ammonium acetate to reduce the hydrogen ion concentration approximately to that of acetic acid. The object is to precipitate the V as lead vanadate in an acetic acid solution. The ammonium acetate solution may be made by mixing 80 cc. of strong ammonia, 100 cc. of water, and 70 cc. of 99 per cent acetic acid.

Heat the liquid containing the lead vanadate precipitate on the steam bath for one hour or more, filter on a tight filter and wash with warm water. Dissolve the precipitate in the least possible quantity of hot dilute (not stronger than 1—3) nitric acid, neutralise as before, add 3 cc. of HNO_3 in excess, add 2 cc. of lead acetate solution and repeat the precipitation of lead vanadate by adding ammonium acetate in excess, filter and add the filtrate to the first one. Reserve the precipitate of lead vanadate for treatment described below. Concentrate the united filtrates from the lead vanadate to about 400 cc., add 10 cc. of strong H_2SO_4 to separate the bulk of the lead (derived from the excess of lead acetate) as PbSO_4 , filter it off and wash with cold H_2O . Neutralise the filtrate from the PbSO_4 with ammonia and add freshly prepared $(\text{NH}_4)\text{HS}$ until the solution is yellow and the uranium and what little lead is present are separated as sulphides. Warm the mixture on a steam bath until the sulphides settle well. Filter and wash slightly with warm water.

Dissolve the precipitate with hot dilute nitric acid (1—2) and collect the solution in a No. 2 beaker, add 5 cc. of H_2SO_4 and evaporate to the appearance of fumes, cool and take up with water, boil and let the small amount of PbSO_4 settle until the solution is cold, filter it off and wash it with very little dilute H_2SO_4 .

Separation of Alumina.—Nearly neutralise the filtrate with ammonia; have the solutions cool (not over 30°) and add powdered carbonate of ammonia in about 2 grms. excess, let the precipitate of alumina settle, filter it off, wash with warm water, and if it appears to be a considerable amount, or is at all yellow in colour, dissolve it in a little dilute H_2SO_4 and reprecipitate with ammonium carbonate as above. Acidulate the filtrate from the alumina with H_2SO_4 , boil thoroughly to expel CO_2 , make the liquid slightly alkaline with NH_4OH while it is hot, and heat on the water-bath until the ammonium uranate collects and settles. Filter and wash with very dilute $(\text{NH}_4)\text{NO}_3$ (2 per cent). Do not allow the precipitate to run dry on the filter after the first washing. Dry the precipitate and ignite it in porcelain, weighing as U_3O_8 . Dissolve the precipitate in HNO_3 and test it with H_2O_2 for vanadium and with $(\text{NH}_4)_2\text{CO}_3$ for aluminium.

Dissolve the lead vanadate in dilute nitric acid, add 10 cc. of H_2SO_4 , and evaporate the mixture until fumes appear. Cool, take up with water, and add fusion solution (see following paragraph), add 10 cc. of concentrated solution of SO_2 to the mixture, boil until the excess of SO_2 is expelled, and titrate the hot solution with potassium permanganate solution. The reduction of the solution by SO_2 is from V_2O_5 to V_2O_4 . It is not necessary to filter out the lead sulphate before boiling to expel SO_2 . The boiling is best done in a large flask. In expelling the excess of SO_2 , it is necessary to boil the liquid for at least ten minutes after the odour of SO_2 can no longer be detected.

The iron precipitate, which was produced by the addition of Na_2CO_3 and H_2O_2 to the original acid solution, may contain vanadium. Ignite it in a platinum crucible and fuse it with Na_2CO_3 , leach the fusion with water, filter, acidulate the filtrate with H_2SO_4 and add it to the main solution before reducing with SO_2 or reduce and titrate it separately if prepared.

For the details of other methods of control one is referred to *Bulletin* 70 of the Bureau of Mines, 1913 and 1914, pp. 82 to 91.

In general, it may be stated that the most prevalent errors in the determination of uranium result in the precipitation of some other material, such as SiO_2 , Al_2O_3 , or V_2O_5 , along with uranium, which would produce a low Ra/U ratio. To guard against the former two possibilities, we have usually redissolved U_3O_8 and passed the solution through a Jones' reductor to determine uranium volumetrically by titration with KMnO_4 .

(To be continued).

POTASH SALTS.

SUMMARY FOR 1913.*

Compiled by W. C. PHALEN, United States Geological Survey, Washington, D.C.

(Continued from p. 221).

ALUNITE AS A SOURCE OF POTASH SALTS.

Composition as Mineral.

The mineral alunite is a hydrous sulphate of potassium and aluminium with the symbol $\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 6\text{H}_2\text{O}$. Theoretically it contains 11.4 per cent K_2O , 37 per cent Al_2O_3 , 38.6 per cent SO_3 , and 13 per cent water. The composition of alunite found at Marysville, Utah, a locality at which the mineral occurs on a considerable scale, as will be seen from the table of analyses that follow, is very close to the composition of the pure mineral as given above:—

Analyses of Alunite from Deposit near Marysville, Utah.

	18.	19.	Dana.
Al_2O_3	37.18	34.40	37.0
Fe_2O_3	Trace	Trace	—
SO_3	38.34	36.54	38.6
P_2O_5	0.58	0.50	—
K_2O	10.46	9.71	11.4
Na_2O	0.33	0.56	—
$\text{H}_2\text{O} +$	12.90	13.08	13.0
$\text{H}_2\text{O} -$	0.09	0.11	—
SiO_2	0.22	5.28	—
	100.10	100.18	100.0

No. 18 is a selected specimen of the supposedly best material. It consists of clear pink, subtransparent, coarsely granular, crystalline rock. No. 19 is a selected specimen of a light pink, very finely granular rock of almost porcelain-like conchoidal fracture and no distinct structure.

Method of Recovering Potash.

Experiments conducted in the laboratory of the United States Geological Survey have shown that on igniting powdered alunite all the water and three-fourths of the sulphuric acid are driven off. When the residue is leached with water, potassium sulphate dissolves and insoluble alumina is left. The average quantity of potassium sulphate leached from the ignited mineral is 17.9 per cent of the original material used. As the coarsely crystallised alunite was found to contain 19.4 per cent potassium sulphate, 92 per cent of the total potash present was obtained by simple ignition and subsequent leaching. According to the laboratory experiments 32.7 per cent of

* From *The Chemical Engineer*, xx., No. 3.

the ignited alunite consists of available potassium sulphate, which may be obtained by leaching and evaporation. The remaining 67.3 per cent is nearly pure alumina. Several foreign deposits of alunite have been successfully worked for the manufacture of alum (B. S. Butler and H. S. Gale, "Alunite, a Newly Discovered Deposit near Marysville, Utah," U.S. Geol. Survey, 1912, *Bull.* 511, 10).

United States Geological Survey Work on Alunite.

There have been incorporated in this chapter in past years notices of all the occurrences of alunite that have been reported and described by members of the United States Geological Survey. Occurrences thus noted are those near (1) Marysville, Piute County, Utah; (2) at five localities in the San Cristobal quadrangle, south-western Colorado; (3) near Bovard, Esmeralda County, south-western Nevada; and (4) in the Palmetto mining district, 5 miles south of Patagonia, Santa Cruz County, Ariz. E. S. Larsen, who described the occurrence in the San Cristobal quadrangle, Colorado, reports the mineral also at five or six different places in the Uncompahgre quadrangle, also in south-western Colorado.

New Occurrence of Alunite in Utah.

Specimens containing alunite were sent to the Survey early in 1914 from the Newton mining district, about 9 miles north-east of Beaver, Beaver County, Utah, by William A. Wilson, of Salt Lake City. The material was said to have been collected from the locality known as Sheep Rocks, situated on the western flank of the same mountain range under geologic conditions similar to those of the occurrence near Marysville.

The material sent to the Survey has been examined by B. S. Butler and found to be a mixture of the minerals alunite and quartz, there being approximately 30 to 40 per cent of the latter. It should be borne in mind that the presence of alunite in the proportion given above is based on results obtained from the examination of a single specimen. Whether further search will develop a considerable body of the mineral is entirely problematical. It is interesting, however, to note, as stated elsewhere in this report, the rather general distribution of alunitisation, as this form of rock alteration may be called.

Attention on the part of the owners and others interested in these and other similar deposits should be given to the interesting results obtained in experiments with alunite as a fertiliser both in the raw and in the roasted form. These results are outlined in another part of this report.

Utilisation of Alunite.

Though the mineral alunite, since attention has been directed to it as a possible source of potash salts and alumina, has been found to be quite widespread in occurrence in certain of the Western States, and has come to be recognised as a rather common form of rock alteration, the Marysville, Utah, deposit is the only one that has been regarded as of any commercial importance up to the present time. The composition of the Marysville mineral has already been indicated.

One of the companies interested in the occurrence near Marysville is the Florence Mining and Milling Co. This company issued a prospectus in 1913 outlining the benefits of potash as a fertiliser and giving some concrete data on the company's holdings and alunite near Marysville.

Certain newspaper reports regarding the future exploitation of the Marysville deposits which have come to the Survey's attention, but which must be distinctly understood as not authenticated by it, are as follows:—

Among the plans for the exploitation of the Marysville alunite is one for the erection of a roasting and grinding plant, which is to be installed in the spring of 1914. Because of the possible injury to the forests from the fumes of the oxides of sulphur given off during the roasting of the mineral, it is thought that the plant will not be per-

mitted in the mountains near the occurrence itself. It is probable, therefore, that it will be built near the Denver and Rio Grande station at Marysville, at which locality the prevailing winds will carry the acid fumes into the barren foothills of the ranges east of the valley. An aerial tram is projected to convey the ore from Cottonwood Canyon to the plant.

Method of Utilising Alunite.—A process for obtaining sulphate of potash and alumina has been devised by H. F. Chappell, and is described in patent No. 1,070,324, dated August 12, 1913. According to the specifications in this patent, sulphate of potash and aluminium oxide are obtained from natural deposits of alum stone, alum rock, and alunite by heating them at a temperature of about 800° to 1000° C. until the aluminium compounds present are converted into insoluble aluminium oxide and the potassium compounds present are converted into potassium sulphate. The latter salt is then extracted by lixiviation.

KELP AS A SOURCE OF POTASH SALTS.

Private Investigations.

The utilisation of kelp as a source of potash salts has been discussed in detail in this chapter in the last two years. In the report for 1911 especially, the results of private investigation, and those of the Bureau of Soils, were outlined. These results will not be repeated here, but the outline of the progress of the work to date, and the more important results which apparently have been derived therefrom, will be given.

The occurrence of potash salts in large amounts in kelp has been known for many years. The experiments of David M. Balch on the Pacific coast kelps began early in 1905 (*Journ. Ind. and Eng. Chem.*, 1909, i., No. 12, p. 777). Balch gives in the articles cited a concise description of the range, relative abundance, life habits, and chemical composition of the three most important giant kelps of the Pacific coast. He also considers their economic value and the practical methods of utilising their products.

Investigations by the Bureau of Soils.

During the spring and summer of 1911 work on the Pacific coast kelps was begun by the Bureau of Soils of the Department of Agriculture. During that year field observations were made on Puget Sound, on the California coast, from Golden Gate to Point Sur, and from Cape Conception to Point Loma. Laboratory investigations were carried out on the material collected. The work was continued during 1912, and as a result there have been prepared maps of the kelp groves covering an area of 230 square miles on the Pacific coast, from Puget Sound in the United States to the Cedros Islands in Mexico. The details of the work accomplished are contained in different publications of the Bureau of Soils, which have appeared in both official and unofficial journals.

During the season 1913 work both in the field and in the laboratory was done by the Bureau. Two parties were engaged in locating and determining the extent and important characteristics of the kelp along the shore line of Alaska; another party investigated on the ground the possibilities of developing a combined fish scrap and kelp industry on Puget Sound and in Alaska. Observations were made at La Jolla and Point Firmin, Cal., and at Friday Harbour, Wash., on the life history of these algæ, especially in relation to cutting and harvesting them.

Three papers—one on the leaching of potash from freshly cut kelp (A. R. Merz and J. R. Lindemuth, *Journ. Ind. and Eng. Chem.*, v., p. 729, September, 1913), the second on the analyses of certain of the Pacific coast kelps (E. G. Parker and J. R. Lindemuth, *Journ. Ind. and Eng. Chem.*, v., p. 287, April, 1913), and the third on the composition of the giant kelps (A. R. Merz, *Journ. Ind. and Eng. Chem.*, vi., p. 19, January, 1914)—appeared during 1913 or early in 1914. From the experi-

ments of Merz and Lindemuth it is shown "that it is a matter of considerable difficulty to obtain a fair average sample of wet kelp," and also "that freshly cut kelp when immersed in sea water does not, at least at first, lose its potash content very rapidly." In a later paper by Merz (*Op. cit.*, p. 19), the conclusions arrived at by Merz and Lindemuth referred to above were corroborated.

(To be continued.)

COMPETITION WITH GERMAN AND AUSTRO-HUNGARIAN TRADE.

AN important Report has been adopted by the Manufacturers' Section of the London Chamber of Commerce relating to competition with German and Austro-Hungarian Trade. A considerable amount of valuable information has been collected on this subject relating to a very large number of industries and a number of constructive and critical suggestions have been received from manufacturers and from merchants.

In cases where manufacturers have intimated that they are open to manufacture new articles hitherto largely imported from Germany and Austria, they have been put into touch with merchants and enquirers for such commodities through the Statistical and Information Department of the Chamber. One of the Appendices to the Report, which has been sent to the Local Government Board, shows that as a result of the dislocation of business caused by the European War and the abnormal conditions of trade there has been a general and substantial decrease in the manufacturing industries, and only a very small increase in certain special trades, but, on the other hand, the number of cases in which business is practically suspended is infinitesimal. Naturally, unemployment has resulted to some extent, and the number of employees joining the colours has not quite counterbalanced the decrease in employment.

In a large percentage of cases supplies of raw material which has previously come from abroad could be obtained in this country or from new sources, and so far as can be ascertained no very great difficulty has been experienced in connection with transport by rail, road, or sea. Industry has been very largely affected by the financial conditions and the reduction in orders both from abroad and from home, but it is not generally considered that orders at home have diminished as a result of the failure of credit but rather from other causes. Various suggestions have been made to assist trade, and special attention is called to the desirability of the bankers being induced to give greater financial facilities to employers of labour and others in connection with the development of existing manufactures and the establishment of new industries in order that the country may be in a position to take full advantage of the change in the economic conditions brought about by the War.

The Emergency Committee of the Manufacturers' Section has been reappointed to give effect to the suggestions relating to allotment of Army contracts, code facilities for cable communications, the relaxation of excise duties on alcohol, Government assistance for firms having large uncollected assets due from belligerent and neutral countries, the re-establishment of foreign exchange operations on a satisfactory basis, and the relaxation of the Factory Acts to allow for more elasticity in the hours and conditions of working arrangements.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 2nd inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Mr. Banister Flight Fletcher was elected a Member.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clix., No. 14, October 5, No. 15, October 12, 1914.

These numbers contain no chemical matter.

Bulletin de la Société Chimique de France.
Vol. xv.-xvi., No. 14, 1914.

Catalysis of Butyric Acid by Thoria.—A. Koehler.—By the study of the transformation of butyric acid into butyrene in presence of thoria, the author has found that the quantity catalysed per unit of time is constant and independent of the rate. It is also independent of the weight of the catalyst, but is a function of the surface presented by the catalyst, and is probably proportional to the surface. It diminishes when the dilution exceeds a certain limit.

Fluorine in Potable Waters.—Armand Gautier and P. Clausmann.—Fluorine exists in all soft waters, but in very small quantities varying from 0.01 mgrm. to 0.6 mgrm. per litre. The waters which are richest in fluorine are those coming from primitive rocks, granites, schists, gneiss, and from regions having no calcareous rocks. When waters originally rich in fluorine flow over calcareous soil they lose their fluorine, owing to its fixation by carbonate and phosphate of lime.

Synthesis of Aldehydes by Zinc Organo-metallic Derivatives.—E. E. Blaise.—By means of the zinc organic derivatives aldehydes can be synthesised by the fixation of the functional group, CHO, on any carbon radicle whatever. Using lactic acid and α -oxyisobutyric acid the author first obtained the formic ethers by the action of acetoformic anhydride, or a mixture of acetic anhydride and crystalline formic acid. The action of thionyl chloride gave the acid chlorides, which condensed with iodide of zinc-propyl to give the cycloacetals. The latter were then hydrolysed by means of oxalic acid, and thus a yield of 80 to 90 per cent of the aldehyde was obtained.

Synthesis of α -Monochloroketones by Zinc Organo-metallic Derivatives.—E. E. Blaise.—To prepare the α -monochloroketones the author condensed an acid alcohol with the chloride of a chlor-acid, and then transformed the acid ether salt thus obtained into an acid chloride. On treatment with the organo-zinc derivative the cycloacetal was obtained and could be split up by hydrolysis to give the α -chloroketone.

Determination of Ethers in Essential Oils.—Jean Nivière.—To determine ethers in essences about 1.5 to 2 grms. of essence are weighed in a 100 cc. flask. A known volume of standard alcoholic potash is added, and the mixture is heated on the water-bath for half-an-hour, a long glass tube being provided as a condenser. After cooling, 50 cc. of water are added to the contents of the flask, and they are titrated with sulphuric acid in presence of phthalein. The author has studied this process, and has found that it gives concordant results. Saponification in a closed vessel is not advisable, as it gives higher values for the amount of ether than are obtained by the open vessel method.

Characterisation of Morphine and Phenols by Uranium Salts.—J. Aloy and Ch. Rabaut.—To detect morphine by means of uranium salts different methods have to be adopted according as the alkaloid is present in the free state or as a salt. In the former case a small quantity of alkaloid is placed in a test-tube, some drops of pure methyl alcohol are added, and then a small crystal of uranium nitrate. On shaking the liquid reddens, the coloration being dependent upon the amount of morphine present. In the second case the salt (hydrochloride) is dissolved in water, and a crystal of uranium acetate or a

few drops of a saturated solution are added. As before, a red coloration appears. The same reaction can be used to show the presence of a free phenolic OH group, and hence to differentiate morphine from other alkaloids of opium or from vegetable bases which do not possess the function.

MISCELLANEOUS.

Wellcome Chemical Research Laboratories.—Dr. Frederick B. Power will retire from the directorship of the Wellcome Chemical Research Laboratories on December 1, in order to return to the United States of America, where, for family reasons, he will make his future home. His period of service dates from the foundation of these Laboratories by Mr. Henry S. Wellcome in the spring of 1896. The high character of the research work carried out in these Laboratories during these eighteen and a-half years by and under the immediate direction of Dr. Power, stands without a parallel in his department of science. It has been truly said that Dr. Power has, during the period of his administration, inaugurated a new era in his field of research in England. Dr. Power will be succeeded by Dr. Frank L. Pyman, whose researches and contributions to chemical science are well known. The character and policy of the Wellcome Chemical Research Laboratories will continue as in the past.

Philippine Journal of Science.—The February number of this journal contains an interesting account of the researches of Messrs. J. R. Wright and O. F. Smith upon the variation of the amount of radium emanation in the atmosphere with altitude and meteorological conditions. The amount of radium emanation was determined by the charcoal absorption method, and was found to be subject to considerable variation, the ratio of the maximum to the minimum being approximately 4:1. It decreases with altitude, and determinations made during fair weather almost invariably give high values, while observations taken after or during heavy rains show a decided decrease. No definite relation has been established between the variation of the amount of emanation and a rising or falling barometer. A decided variation between day and night exposures has been found, the ratio of the average for the night to that for the day being approximately 2 to 1.

London Chamber of Commerce.—A meeting of the Naval and Military Defence Standing Committee of the London Chamber of Commerce was held recently, when the Deputy-Chairman, Mr. Stanley Machin, presided, in the unavoidable absence of Lord Roberts. The following resolutions were adopted:—

That this Committee, while recognising the patriotism of individual employers, urges upon the business community the importance of continuing until the end of the war to assist by every means in their power the enrolment for the war of further recruits for Lord Kitchener's army in view of the vital attack against the security and existence of the Empire.

That, having regard to the need for strengthening Home defences, this Committee strongly supports the movement initiated in connection with the Central Association of Volunteer Training Corps for enabling the civil population to gain instruction in drilling and the use of arms.

That, in view of the experience which has been gained in France and Belgium as to the action of enemy spies, and, while appreciating the precautionary steps already taken by the British Government in the United Kingdom, this Committee is of opinion that more stringent precautions should be taken in the case of naturalised British subjects of enemy origin, and that the segregation of born aliens, whether naturalised or not, should not be confined to those of military age.

Essay Competition on Radium.—Having regard to its remarkable chemical and therapeutic properties there is no substance more worthy of experimental study than radium, and we are pleased to notice that in the county of Dorset that study is being stimulated by an essay-writing competition promoted by the Dorset Natural History and Antiquarian Field Club. The club announces that the Cecil Medal (of solid silver) and a prize of £10 will be awarded for the best essay, written by a Dorset competitor—Dorset by birth or residential qualification—between the ages of 17 and 35, on the subject of "Radium: Its Present Position, Supply, and Cost, with any Recent Discoveries on its Curative Effects." Full particulars may be obtained from Mr. H. POUNCY, *Chronicle* Office, Dorchester. (See notice in advertising columns).

Iron and Steel Institute.—The Hadfield Research Prize.—A Research Prize of the value of £200 has been placed by Sir Robert A. Hadfield, F.R.S., Past President, at the disposal of the Council of the Iron and Steel Institute, to be awarded by the Council for original research work on the subject of the Different Forms or Combinations of Carbon in Iron, Steel, and Alloys of Iron with other Elements. Competition for the prize is open to metallurgists, chemists, and others interested in Metallurgy, and it is proposed that the prize shall be awarded at the Annual Meeting of the Institute in May, 1916, for the best report presented before February 1, 1916. Sir Robert Hadfield is also prepared to offer a second prize for the report next in merit to the one which gains the first prize provided it is adjudged to be a really meritorious paper. It is not desired to limit the scope of the research too closely, but it is suggested that the work should be in continuation of, or based upon, the work of previous investigators, such as Jullien, Abel, Müller, Ledebur, T. Sterry Hunt, Akerman, Arnold, E. D. Campbell, Hogg, Parry, and others. The object of the Research Prize is to stimulate the study of carbides in iron and iron alloys generally, also with a view to discovering the best method of determining the forms and combinations in which carbon occurs in iron and steel. These carbides are now spoken of by metallurgists in a general way, as sub-carbides, carbides, or double carbides. It is very desirable to define the composition of these more accurately and to ascertain whether other carbides exist which have hitherto not been identified. The study of the molecular constitution of the carbides will also fall within the range of the investigation, and, in this connection, attention may be directed to previous researches on particular combinations of carbon or forms of carbide. For instance, it would be of interest to determine whether the ordinary carbide is Fe_3C , Fe_6C_2 , or some other combination. If so, what is its nature and molecular constitution? The foregoing is a general direction which should guide intending participants in this research. It is hoped that the results obtained will throw much light on the cause of hardness of steel, also on the nature and form of carbon combinations with iron and its alloys. Intending competitors should communicate, in the first place, with Mr. G. C. LLOYD, Secretary of the Iron and Steel Institute, 28, Victoria Street, London, S.W.

MEETINGS FOR THE WEEK.

THURSDAY, 12th.—Royal Society. "Analyses of Agricultural Yield—Part I., Spacing Experiments with Egyptian Cotton," by W. L. Balls and F. S. Holton. "The Fixation of Arsenic by the Brain after Intravenous Injections of Salvarsan," by J. McIntosh and P. Fildes. "Production of Anthocyanins and Anthocyanidins," by A. E. Everest. "Living Observations on the Life-cycle of a New Flagellate *Helkesimastix faecicola*, together with Remarks on the Question of Syngamy in the Trypanosomes," by H. M. Woodcock and G. Lapege. "Antagonistic Action of Carbon Dioxide and Adrenaline on the Heart," by S. W. Patterson.

FRIDAY, 13th.—Alchemical, 8.15. "The Movement of Alchemical Research in France—Actual Traces of Transmutation," by W. de Kerlor.

— Physical, 8.

THE CHEMICAL NEWS.

VOL. CX., No. 2868.

THE ABSORPTION OF LIGHT BY WATER CHANGED BY THE PRESENCE OF STRONGLY HYDRATED SALTS, AS MEASURED BY MEANS OF THE RADIO-MICROMETER. BEARING OF THE RESULTS ON THE SOLVATE THEORY OF SOLUTION.

By E. J. SHAEFFER, M. G. PAULUS, and HARRY C. JONES.

(Concluded from p. 224).

The observations are plotted in curves 1 to 12. The ordinates are percentage transmission and the abscissæ are wave-lengths.

The light curves in every case represent the transmission of water. The heavy curves the transmission of the solution. The relation which manifests itself from these data and curves is that at the minimum of transmission, the curve for the solution, with one exception, $\text{Zn}(\text{NO}_3)_2$, is always above the curve for the transmission of water. This means that at the maximum absorption the solution is more transparent than pure water even where the absorption band is not appreciably shifted.

The solutions of a number of salts are more transparent in pure water for all the wave-lengths studied. In other cases there is a decided shift of the absorption band of the solution towards the red, in which case the two curves may cross.

The general relation brought out by Guy, Shaeffer, and Jones (*Diese Zeit.*, 1913, xiv., 278), that solutions of salts which hydrate only slightly have essentially the same absorption as pure water, comes out again as the result of our repeating their work with improved apparatus and method.

Also the relation pointed out in the earlier work that solutions of salts with large hydrating power, such as magnesium chloride, magnesium bromide, magnesium sulphate, calcium chloride, zinc sulphate, and zinc nitrate, are more transparent for many wave-lengths than pure water, having the depth of the water in the solution in question.

The greatest differences between the absorption of water and of the solution manifest themselves where the absorbing power of water is the greatest. This difference is sometimes as much as 40 per cent.

In a short article which appeared in *Diese Zeit.* (1913, xiv., 660) G. H. Livens calls attention to the supposed fact that in a preliminary paper (*Diese Zeit.*, 1913, xiv., 278) from this laboratory on this subject, some of the results were in accord with certain consequences deduced from the Lorentz theory of dispersion and absorption of light; and on the basis of this he has indicated that the earlier experimental work from this laboratory can be explained in an entirely different manner from the interpretation which we then gave.

Four of the curves published in the first paper seemed to accord with the deductions of Livens; the remaining two certainly do not, and furthermore, in our opinion, he did not give the case quite fair consideration in that he seemed to have disregarded the fact that the solvent and solution curves for three non-hydrated salts are practically identical. The earlier work clearly showed that it was only in the case of the hydrated salts that marked differences were to be noted between the transmissions of solvent and solution.

The four curves in question have been worked out again, duplicate measurements being made.

These most recent results seem to justify us in retaining our original explanation. We are now fairly certain that none of our curves can be explained by the above-mentioned deductions of Livens. Why these more recently obtained curves are slightly different from those published earlier will be explained below.

According to Livens the maximum absorption of the solvent is to be represented by—

$$\mu_0 \chi_0 = \frac{\rho'}{2n_{0n}'} ,$$

while that of the solution is—

$$\mu \chi = \frac{\mu_0 \chi_0}{(1 - aA)^2} ,$$

A being

$$\Sigma \frac{e^2}{k - mn_0^2} .$$

In all of the cases studied, except the 1μ band for zinc nitrate, the maximum absorption of the solution is consistently less and in many cases decidedly less than the maximum absorption of the solvent. This being the case, it is necessary to assume that A is less than zero, and this demands a shift of the solution band towards the violet. There is not the slightest indication that any of the bands are displaced towards the violet; on the contrary, the slight displacement which occurs at the centre of the band is certainly towards the red in all cases.

It will thus be seen that our experimental results for the hydrated salts are not at all interpretable by the deductions of Livens, which furthermore fail to account for the fact that there is no appreciable difference between the transmissions of the solutions and solvent for the non-hydrated salts.

It appears to us reasonable to think that the vibration frequency of the electrons is not the same for combined water as it is for pure water. Why the factor A has such a marked effect for hydrated salts and not for non-hydrated salts of nearly the same concentration, seems to be a difficult matter to explain on any basis other than the solvate theory of solution.

It will be noticed that in nearly all cases, the difference between the maximum absorption of the solvent and of the solution is small, and in this work, so inherently difficult, involving as it does so many distinct and separate operations, it is only by exercising the very greatest care that consistent results can be obtained. Due to this fact it is not wise to base any final conclusions on such uncertain ground alone as the maximum absorption of the solvent and the solution, especially when the work was just begun and the cases studied at that time so few in number. Why the maximum absorption of the solvent was higher in four of the curves first published is probably due to either one or the other of the following reasons:—It is not an easy matter to plate with gold the brass cells and the exposed portions of the Woods metal which holds the ends in position in such a manner that the concentrated, and some cases strongly hydrolysed, solutions would not react with some of the metallic constituents, giving rise to streamers in the solution and to a slight opalescence. This caused much annoyance during the early work on this problem; but we can confidently say that during the work, the results of which are herein recorded, every solution studied remained perfectly clear. In case any turbidity developed the cells were at once replated and the work repeated.

The effect of an opalescence in the solution would, of course, increase the absorption and cause the solution to be less transparent at the centre of the band. In filling the cell with the solution there is great danger of contaminating the glass-ends with the dissolved substance. It was found that an almost invisible film of the dissolved substance on the glass-ends of the cell would increase the absorption 5 per cent. These films are not sufficiently removed by ordinary methods of cleaning. Of course, if the cells were filled with water, we would have no such

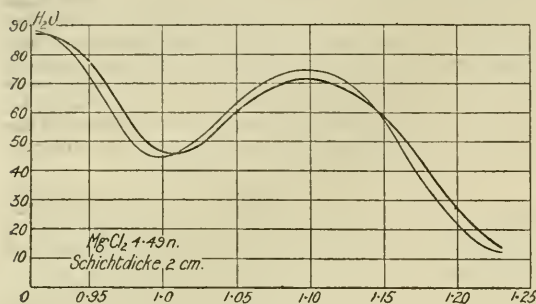


FIG. 1.

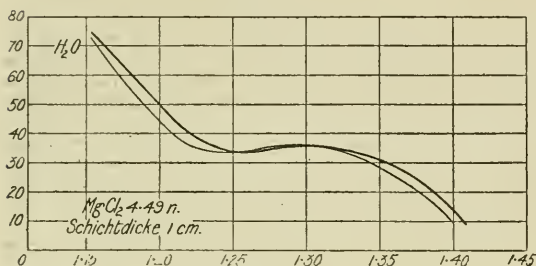


FIG. 2.

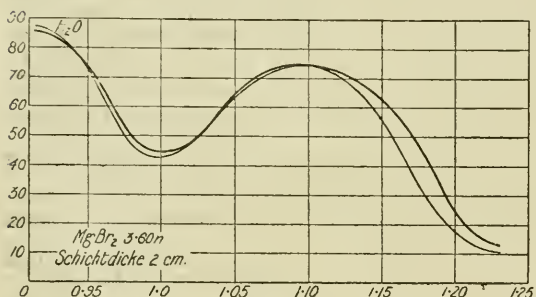


FIG. 3.

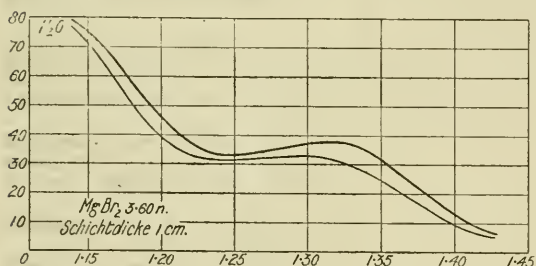


FIG. 4.

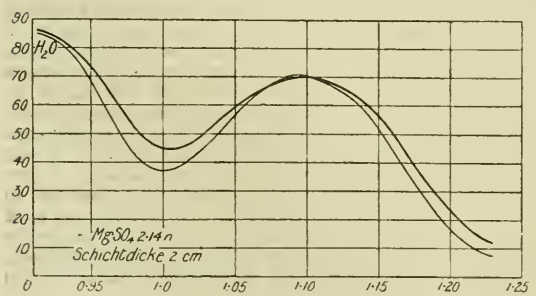


FIG. 5.

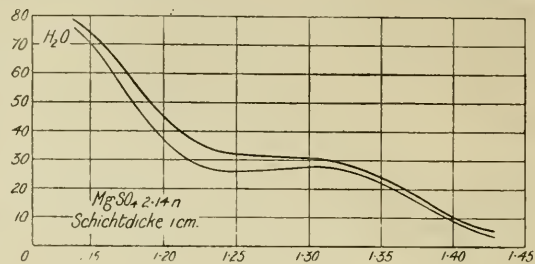


FIG. 6.

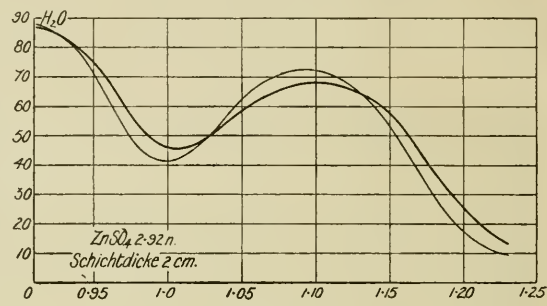


FIG. 7.

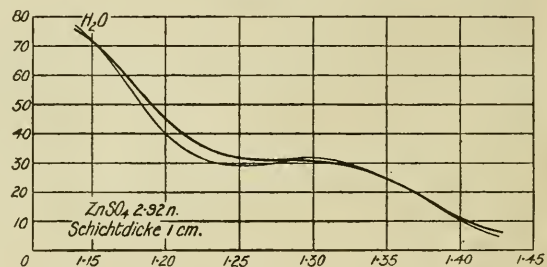


FIG. 8.

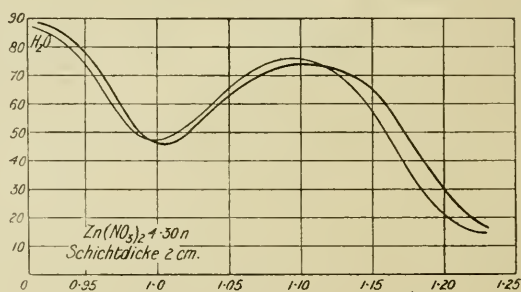


FIG. 9.

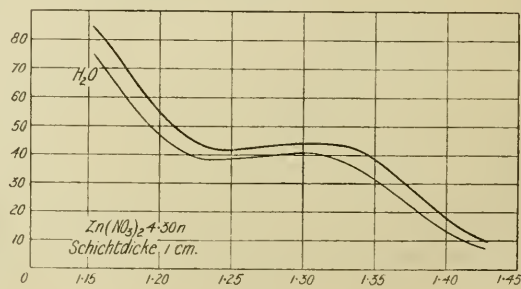


FIG. 10.

effect as that referred to above for solutions. In all this work special care was taken to have the glass-ends of the cells thoroughly cleaned.

To summarise: The work herein recorded shows that aqueous solutions of non-hydrated salts have very nearly the same absorption as pure water, having the same depth as the water in the solution. That strongly hydrated salts have in general much less absorption than a layer of

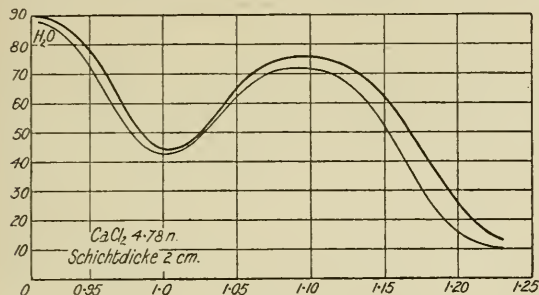


FIG. 11.

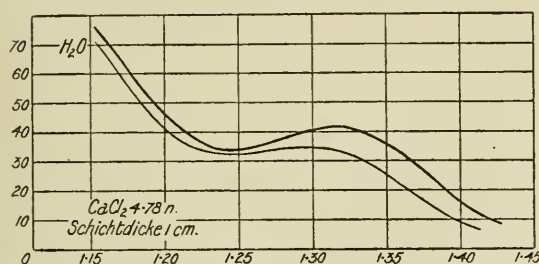


FIG. 12.

water equal in depth to the water in the solution. A number of new examples have been added to those recorded in the earlier paper.

The attempt of Livens to explain these facts on grounds other than the solvate theory of solution can not be regarded as successful for reasons pointed out above.

Work is now in progress on the effect of solvation on the absorption spectra of solutions in solvents other than water and in mixed solvents.

(This investigation was carried out with the aid of Grants awarded H. C. Jones by the Carnegie Institution of Washington).

AIR OZONATION.*

By MILTON W. FRANKLIN.

THE subject of air ozonation may be divided into three heads:—I. Ozone as an adjunct to ventilation; II. Destruction of odours from industrial plants such as glue factories, fertiliser plants, slaughter-houses, fish marts, &c.; III. Adjunct to refrigeration in the practice of cold storage and food preservation.

I. Ventilation.

The application of ozone to ventilation has attracted much attention recently owing to the publication of a multitude of conflicting opinions concerning its merits. This confusion is due to several circumstances. In general, the proponents of ozone have claimed too much and have advanced many contentions, either insufficiently supported or in the very nature of things insusceptible of

proof. On the other hand, the opponents of ozone have attacked these claims with great energy and often have gone so far as not only to deny any usefulness whatever to ozone, but positively to affirm its harmfulness and dangerous character. In any cases the attacks on ozone have been directed against imaginary claims that were never made, and much of the evidence against ozone is based on laboratory experiments which bear little or no resemblance to actual working conditions and therefore can scarcely be considered as authentic.

A careful and unbiased investigation of all the evidence accessible in the extant literature in connection with the theory and principles of ventilation hygiene must result in the conviction that ozone, properly applied, is capable of advancing greatly the art of ventilation, and that it is incapable of harming persons exposed to its influence.

At the Ninth Congress for Heating and Ventilating held in Cologne in June, 1913, two notable papers were read—one by Prof. Czapski (*Gesundh. Ing.*, August 2, 1913), and the other by L. Von Kupffer (*Ibid.*, Aug. 16, 1913, p. 605), which presented in detail the present status of the question, and which elicited the following comment from Dr. Ing. H. Rietschel, the honorary president of the Congress:—

" . . . We have heard with conviction that ozone has been used in numerous cases with the best of results for ventilating plants and that it can be used for such purposes; also that in the diluted state in which it is to be used it cannot be considered as being harmful. We shall, therefore, devote our undivided attention to ozone and its application for ventilating purposes."

The subject of ozone in ventilation was treated by the present writer in a paper presented at the Fourth International Congress on School Hygiene (*Heating and Ventilating Magazine*, N.Y., Oct. and Nov., 1913, vol. x., Nos. 10 and 11), in which were described some experiments which demonstrated that many odours arising from organic sources were destroyed and not masked by ozone. It was shown that—

1. Ozonised air does not merely mask offensive odours of varied nature, but that it actually destroys them.
2. The odours of some common food materials (onions, garlic, and limburger cheese) are destroyed by ozonised air.
3. The odours resulting from decayed raw food materials, fish, eggs, meat, and oysters, are destroyed by ozonised air.
4. The offensive odours of fertilisers are destroyed by ozonised air.
5. Several definite chemical compounds which contribute to the odour of fæces, perspiration of feet, rancid butter, sauerkraut, and limburger cheese, namely, skatol, valerianic acid, and butyric acid, are also destroyed by ozonised air.
6. The persistent odour of tobacco smoke as absorbed by the clothing is destroyed by ozonised air, and the yellow colour produced by blowing smoke through cloth is bleached by ozone.

The accompanying table presents some of the materials upon which the experiments were performed.

According to the modern theory of ventilation, the only baneful factors in "vitiating" air are heat, moisture, and odours. If the air is stagnant and motionless its powers to absorb heat and water are not utilised fully; hence, a fan which circulates the air generally adds much to the comfortableness of a poorly ventilated space. The ancient beliefs that excess of carbonic acid gas and deficit of oxygen accounted for the distress attendant upon inadequate air supply have been dispelled by the published labours of Haldane, Hill, Pfuegge, and others. It has been shown that in the worst cases the available oxygen is far in excess of the demand and that CO_2 is harmless in the concentrations likely to be met. The conviction once prevalent that organic "crowd poisons" were the guilty factors likewise has been abolished. Billings, Mitchell, and Bergey ("Composition of Expired Air and its Effect

* From *Journal of Industrial and Engineering Chemistry*, vi. No. 10.

Odour from—	Odour before treatment with ferrous sulphate solution.		Odour after treatment with ferrous sulphate solution.	
	With air.	With ozone.	With air.	With ozone.
Onions	Strong onion	Strong ozone	Strong onion	None
Garlic	Strong garlic	"	Strong garlic	"
Limburger cheese ..	Strong Limburger	"	Strong Limburger	"
Decayed fish.. ..	Very offensive	"	Very offensive	"
Decayed eggs	"	"	"	"
Decayed meat	"	"	"	"
Decayed oysters	"	"	"	"

upon Animal Life," Smithsonian Inst., 1895) have added much to the knowledge of this aspect of ventilation. The most recently demolished belief was that bacteria existed as a menace in rebreathed air. The works of Pfluegge (*Zeit. f. Hyg. u. Infekt. Krankh.*, xlix., 363), Chapin ("Sources and Modes of Infection," p. 314), Doty (*Med. Record*, N.Y., Nov. 2, 1912, p. 891), and of Winslow and Robinson, have fairly disproven this contention.

The modern practice of ventilation, then, clearly is concerned only with absorbing the almost invariable quantity of heat produced per capita of room occupants, of removing the moisture transpired, and of destroying the odours generated and which are due to the presence of people, animals, and organic substances, including food-stuffs, especially when in a state of putrefaction.

Heat and moisture absorption have received weighty consideration from the engineering profession and may readily be accomplished with accuracy and certainty in any given set of conditions. Odour elimination, by no means the least important, may be accomplished best through the agency of ozone. Supplying too great an amount of air in a ventilating system constitutes an engineering and hygienic error as well as does supplying too little air. Correct engineering practice consists in accomplishing an end in the least costly manner compatible with correct performance of function; and too much air means dangerous draughts, waste, and inefficiency. Ozone renders possible the elimination of odours which often cannot otherwise be removed at all, or possibly only by the providing of a prohibitive excess of air with the attendant probability of draughts and low economy. But primarily, ozone is most useful in those myriad instances where idealised ventilation systems are simply beyond the question. In these all too numerous, though unfortunately inevitable places, where perfect ventilation is impossible, ozone will produce a condition of the air unattainable by any other known means. It imparts a freshness and "tang" to the air, rendering it comparable with that in the most favoured natural localities.

Ozone in general destroys and does not mask organic odours as has been shown above.

It remains then only to know that ozone is inoffensive and incapable of harming persons breathing it, in such quantities as are used in ventilation, before justifying and recommending its use.

Cramer (quoted from Czaplewski, *loc. cit.*) stated at the Frankfurt Congress for Heating and Ventilating—

"In earlier times we assigned to ozone a poisonous influence on animal organisms, while recent investigations have shown that the ozone is poisonous only when made chemically and not pure. A mixture of chemically pure ozone with atmospheric air can, if the percentage of ozone is not too concentrated, never hurt an organism, as statements from doctors and scientists show. Only in very concentrated form does it attack the lining of the mucous membrane."

No single instance of harm to a person from the proper use of ozone in ventilation has been recorded, but, on the contrary, all adverse opinions have been deduced, by inference, from laboratory experiments performed with very high concentrations, while all efforts to produce harm experimentally with weak ozone have failed. Jordan and Carlson report that twenty-six animals, exposed for fourteen days, during nine hours each day, to concentra-

tions high enough to cause irritation of the eyes and nose, suffered no ill effect whatever. Hill cites the cases of the numerous workers in the London underground tubes, who have shown no ill effect in three years. Gminder cites the unharmed workers in the spinning mills at Reutlingen. Erlwein (*Zeit. f. Sauer u. Stickstoffindustrie*, 1913, Nos. 7 and 8) says—

"It is a fact at any rate that there have never been proven cases of sicknesses of a serious character due to breathing ozone air. Special attention is called to a large water sterilisation plant operating for more than ten years, where the working force is constantly moving in an atmosphere which is more strongly mixed with ozone than is ever found in actual ozone ventilation installations. There has never been a case where these persons have been forced to be on sick-leave due to the high ozone concentrations in the plants."

Numerous similar instances of prolonged proper use of ozone without a single complaint are in existence.

Efforts to disinfect occupied rooms have shown that ozone, in concentrations sufficient to produce sterility of the cultures, is irritating to the mucous membranes of the respiration tract and in fact will produce death in guinea-pigs, but as pointed out above, sterilisation of atmosphere has little sanitary value and it must be remembered that no known method of room disinfection can be practised in the presence of room occupants. Sulphur dioxide, hydrocyanic acid, and formaldehyde would produce death in guinea-pigs more rapidly than would ozone. It has been shown that ozone in high concentrations is a local mechanical irritant, but there is no evidence to justify the opinion that it is injurious in low concentrations.

Toxicologists recognise two distinct classes of poisons, namely, physiological or chemical poisons and mechanical poisons. The former act by being absorbed into the system and causing trains of phenomena through the nervous mechanism; the latter act merely by causing local destruction of the tissues with which they come into direct contact. Strychnine is an example of a chemical poison; its action is dependent only on the quantity ingested and is wholly independent of its concentration. One grain administered internally will cause death, whether it be taken pure or copiously diluted with water. An example of a mechanical poison is sulphuric acid; its only action is a local destruction of bodily tissues, and a quantity which would cause death, if administered concentrated, might be taken with impunity when accompanied by a sufficient diluent. Ozone has been shown to be a mechanical irritant, but to deduce the result that because strong ozone is harmful, weak ozone also must be harmful, is equivalent to arguing that because 50 per cent oxygen breathed for a certain period will cause death from inflammation and œdema of the lungs, 20 per cent oxygen, such as we inspire at every breath, is also poisonous.

Experiments conducted by Jordan and Carlson to determine whether or not ozone in low concentrations, somewhat higher than might be used in ventilation, is harmful, have resulted in the following conclusions—

"All the animal groups showed some increased body weight, but the increase during the ozone period is practically the same as during the control period. Slight differences are of no significance. Hence, as regards appetite and body weight, the results of the tests are negative, the ozone appearing to have neither a favourable

nor an unfavourable influence. This applies also to the general conditions of the animals. The cats did not seem disturbed, even when the ozone concentration caused some restlessness in the rabbits, guinea-pigs, and rats. In all other respects the animals appeared to be normal."

This is a convincing demonstration of the harmlessness of even too high ozone concentrations. The animals were exposed for fourteen days to ozone, following a period of fourteen days confinement for control observation, but in spite of the prolonged close confinement and extremely inadequate ventilation (sixteen cubic feet per hour per animal), they thrived as well during the second fourteen days with rather too strong ozone as during the first fourteen days.

So far as is definitely known, the value of ozone in ventilation is not due to any beneficial effect upon the human economy but to the circumstance that it destroys much that may be objectionable or harmful in foul air. The air is not better because it contains ozone but because this ozone signifies the absence of such organic effluvia as otherwise would be obnoxious.

The well-established fact that ozone is a powerful germicide in the presence of water has led to much experimentation and speculation on its possible power of destroying the bacteria in the air. Wyssokowitz (*Mitt. a. d. Bremer Heilsanstalt*, Wiesbaden, 1890) experimented with chemically formed ozone and found a diminution in the air bacteria, but owing to the many possible errors in his method of procedure his results are frankly admitted to be of little value. He attributed the effect observed to the simultaneous formation of acid, which rendered the soil unsuitable for the growth of bacteria. Froelich (*Electrotech. Zeit.*, 1891, p. 340) found some diminution in air bacteria with strong ozone. Sonntag (*Zeit. f. Hygiene*, viii., 1890) found no effect of ozone in low concentrations on dry bacteria, but with extremely high concentrations (13.5 grms. per cbm.) the bacteria were destroyed. Konrich also obtained negative results with cultures dried on strips of filter paper and on glass-rods. Labbé and Oudin produced diminution in the bacterial count, but they admit that their results are of little importance, owing to possible sources of error.

Bail (*Prag. med. Wochenschr.*, 1913, No. 17, p. 216) has experimented quite extensively and states—

"Even strong ozonisation of the enclosed air with circulation never allowed the beginning percentage of the air as regards bacteria to be reduced in a conclusive manner. The bacteria in the air were determined either on open agar plates or else by passing known quantities of air through gelatin. Passing air, ozonised as much as possible in the apparatus, through tubes having powdered bacteria or through loose sand containing bacteria, gave no conclusive indication of an effective action of the ozone on the bacteria. Experiments to change the humidity of the air by evaporating water during ozonisation and circulation produced no changes in the results."

Jordan and Carlson found little or no effect on plated and dried cultures with low ozone concentrations, but in four tests on the bacteria suspended in the air, three showed an average decrease of 53 per cent and one showed an increase of 10 per cent. The writer has shown a decrease in the bacteria suspended in the air, but the ozone concentration probably was relatively high.

The general evidence of laboratory experimentation seems to indicate that low concentrations of ozone, at least, have no consistently demonstrable action on dried bacteria, whether in cultures or floating in air. On the other hand, there is a considerable amount of evidence to the effect that in storage cellars and similar places the growth of fungi, moulds, and similar micro-organisms is impeded, if not totally repressed, by even weak ozone concentrations applied for prolonged periods. A possible explanation is afforded in the work of Trillat (*Eighth Intern. Cong. Appl. Chem.*, xix., 71), who has shown—

"That the transport of pathogenic microbes in the air is effected especially by the damp which contains, in an in-

finitesimal state, traces of gas-aliments. Moreover, it would seem that the air, when it fulfils certain conditions of dampness, of chemical composition, of temperature, and of age of microbes, is capable of being fertilised directly by the contact of a microbial source. Up till now it was thought, according to numerous observations, that for microbes to be transported by the air it was necessary to project them into it by some mechanical action, such as pulverisation or any other means, the effect of which would be to detach them from their support. Contrary to this notion, Trillat and Fouassier have established experiments demonstrating that when the superposition of certain factors takes place, the sowing of the air is performed in the same manner as that of a bouillon culture, merely by the play and movement of the invisible vesicles which constitute the humidity of the air. In an infinitely feeble volume of about one hundred-thousandth of a cubic millimetre these tiny drops are uninfluenced by the action of the force of gravity. They are always mobile under the influence of the least variation of temperature. M. Trillat and Fouassier have shown how the contamination of the air takes place in a closed and tranquil space, without the intervention of the presence of dust or of any mechanical means, as was believed up to the present time."

It seems probable that the gradual lessening in the bacterial count in the air of places that have been ozonised for some time is due, not to direct influence of ozone on the bacteria, but to the alteration in the air as a culture medium and also to the fact that the myriad cracks and crevices in the walls, ceilings, hangings, furniture, &c., which harbour cultures that constantly supply bacteria in the air, are gradually exhausted. This would account for the discrepancy between laboratory tests of brief duration and actual prolonged trials.

(To be continued.)

THE RADIUM : URANIUM RATIO IN CARNOTITES.*

By S. C. LIND and C. F. WHITEMORE.

(Concluded from p. 231).

VIII. Experimental Data for Carnotites.

THE order of numbering is one of convenience only, but the same numbers have been used for the same ores throughout the paper.

Ra values consisting of the sum of two determinations refer to the "complementary" method; those without designation refer to method of total emanation by solution in one operation; ignition methods are designated as such.

No. 1. A sample from 65 lbs., Cripple Creek claim, Long Park, Paradox Valley, Colorado. Per cent U_3O_8 : 2.10, 2.08, 2.12; average, 2.095 = 1.78 per cent U. Average per cent V_2O_5 , 2.53. Ra per grm. $\times 10^9$: 5.94, 6.11, and 5.99 (ignition method). Average, 6.02×10^{-9} grms. Emanating power = 29.6 per cent. Ra/U = 3.38×10^{-7} .

No. 2. A small sample from the "Rajah" claim, Roc Creek, Paradox Valley, Colorado. Per cent U_3O_8 : 33.19, 33.24; average, 33.22 = 28.18 per cent U. Average per cent V_2O_5 , 14.05. Ra per grm. $\times 10^8$: $1.50 + 8.71 = 10.21$, $1.67 + 8.34 = 10.01$, $1.76 + 8.44 = 10.20$; average, 10.14×10^{-8} grms. Emanating power = 16.2 per cent. Ra/U = 3.59×10^{-7} .

No. 3. A small sample from "Black Fox" claim, Bull Canon, south of Paradox Valley, Colorado. Per cent U_3O_8 : 1.63, 1.57, 1.60, 1.58; average, 1.595 = 1.35 per cent U. Average per cent V_2O_5 , 5.22. Ra per grm. $\times 10^9$: $2.15 + 2.06 = 4.21$, 4.29, 4.30, 4.23 (ignition); average, 4.26×10^{-9} grms. Emanating power = 50.5 per cent. Ra/U = 3.16×10^{-7} .

* Published by permission of the Director of the Bureau of Mines, U.S.A. From the *Journal of the American Chemical Society*, xxxvi., No. 10.

No. 4. A small sample from "Florence" claim, Long Park, Paradox Valley, Colorado. Per cent U_3O_8 : 23.54, 23.42; average, 23.48 = 19.92 per cent U. Average per cent V_2O_5 , 10.63. Ra per grm. $\times 10^8$: $1.404 + 5.861 = 7.27$, $1.166 + 6.082 = 7.25$, 7.33 (ignition). Average, 7.28×10^{-8} grms. Emanating power, 17.7 per cent. $Ra/U = 3.66 \times 10^{-7}$.

No. 5. Small sample from a Curran claim, Long Park, Paradox Valley, Colorado. Per cent U_3O_8 : 24.03, 23.43, 24.75, 24.37; average, 24.25 = 20.60 per cent U. Average per cent V_2O_5 , 13.51. Ra per grm. $\times 10^8$: $2.18 + 2.77 = 4.95$, $2.36 + 2.62 = 4.98$, 4.95, 4.97 (ignition); average, 4.96×10^{-8} grms. Emanating power, 45.8 per cent. $Ra/U = 2.41 \times 10^{-7}$.

No. 6. A small sample of a concentrate prepared by a method which may have affected its Ra/U ratio. Hence the data of No. 6 are not included in Table IV. Per cent U_3O_8 : 9.20, 9.05. Average, 9.125 = 7.74 per cent U. Average per cent V_2O_5 , 10.08. Ra per grm. $\times 10^8$: 2.166, 2.167, 2.184 (ignition); average, 2.17×10^{-8} grms. Emanating power = 30.4 per cent. $Ra/U = 2.80 \times 10^{-7}$.

No. 7. Small sample from "Florence" claim, Long Park, Paradox Valley, Colorado. Per cent U_3O_8 : 3.16, 3.17, 3.23, 3.19; average, 3.185 = 2.70 per cent U. Average per cent V_2O_5 , 4.82. Ra per grm. $\times 10^8$: $4.26 + 6.35 = 10.61$, 10.86, 10.58, and 10.60; 10.94 (ignition); average, 10.72×10^{-8} grms. Emanating power = 39.7 per cent. $Ra/U = 3.97 \times 10^{-7}$.

No. 8. Sample of 3016 lbs. from a Cummings claim, Bull Canon, south of Paradox Valley, Colorado. Per cent U_3O_8 : 4.78, 4.72, 4.62, 4.61; average, 4.68 = 3.97 per cent U. Average per cent V_2O_5 , 4.10. Ra per grm. $\times 10^8$: $4.38 + 8.93 = 13.31$, $4.45 + 8.50 = 12.95$, 12.42, 12.90 (ignition), 13.67; average, 13.05×10^{-8} grms. Emanating power = 33.9 per cent. $Ra/U = 3.29 \times 10^{-7}$.

No. 9. Sample of 29,118 lbs. from the same locality as No. 8. Per cent U_3O_8 : 1.52, 1.57, 1.48; average, 1.523 = 1.29 per cent U. Average per cent V_2O_5 , 4.00. Ra per grm. $\times 10^8$: $1.052 + 3.294 = 4.35$, $0.719 + 3.500 = 4.22$, 4.43, 4.41 (ignition); average, 4.35×10^{-8} grms. Emanating power = 20.4 per cent. $Ra/U = 3.42 \times 10^{-7}$.

No. 10. Sample of about 4000 lbs. from the same locality as No. 5. Per cent U_3O_8 : 2.45, 2.35, 2.48; average, 2.40 = 2.04 per cent U. Average per cent V_2O_5 , 5.27. Ra per grm. $\times 10^8$: 7.23, 7.40, 7.30 (ignition); average, 7.31×10^{-8} grms. Emanating power = 29.0 per cent. $Ra/U = 3.58 \times 10^{-7}$.

No. 11. Small sample from Melrose claim, Green River District, Utah. Per cent U_3O_8 : 4.14, 4.11, 4.12, 4.16; average, 4.13 = 3.50 per cent U. Average per cent V_2O_5 , 5.07. Ra per grm. $\times 10^8$: $4.83 + 5.74 = 10.57$, $5.05 + 5.73 = 10.78$, 11.12, 10.87 (ignition), 11.41; average, 10.95×10^{-8} grms. Emanating power = 45.1 per cent. $Ra/U = 3.13 \times 10^{-7}$.

[No. 12. (Standard) pitchblende from Kirk Mine, Gilpin Co., Colorado. Per cent U_3O_8 : 76.40, 76.58; average, 76.50 = 64.9 per cent U. Ra per grm.: 2.16×10^{-7} (calculated from Heimann and Marckwald's (*loc. cit.*) Ra/U ratio 3.328×10^{-7} , also in close agreement with a sample of analysed pitchblende of known radium content from Boltwood). Emanating power, 2.7 per cent by two determinations of 5.98 and 5.73 $\times 10^{-9}$ curies, respectively.]

No. 13. Sample of a carload lot (calculated 30 tons) from the claims of the Crucible Steel Co., Long Park, Colorado. Per cent U_3O_8 : 2.74, 2.82; average, 2.78 = 2.36 per cent U. Average per cent V_2O_5 , 4.67. Ra per grm. $\times 10^8$: $3.51 + 4.32 = 7.83$ (ignition), 7.89; average, 7.86×10^{-8} grms. Emanating power = 44.7 per cent. $Ra/U = 3.34 \times 10^{-7}$.

No. 14. Sample of carload lot (calculated 25 tons) from the same locality as No. 13. Per cent U_3O_8 : 3.91, 3.95; average, 3.93 = 3.33 per cent U. Average per cent V_2O_5 , 5.12. Ra per grm. $\times 10^8$: $3.90 + 7.19 = 11.09$, 11.09; average, 11.09×10^{-8} grms. Emanating power = 35.2 per cent. $Ra/U = 3.33 \times 10^{-7}$.

No. 15. Sample of a carload lot (calculated 20 tons)

from same locality as No. 13. Per cent U_3O_8 : 2.85, 2.82; average, 2.835 = 2.41 per cent U. Average per cent V_2O_5 , 4.72. Ra per grm. $\times 10^8$: $3.488 + 4.467 = 7.955$, 8.076; average, 8.02×10^{-8} grms. Emanating power = 43.4 per cent. $Ra/U = 3.33 \times 10^{-7}$.

No. 16. Sample of a carload lot (calculated 22 tons) from same locality as No. 13. Per cent U_3O_8 : 2.52, 2.54; average, 2.53 = 2.16 per cent U. Average per cent V_2O_5 , 3.75. Ra per grm. $\times 10^8$: $3.191 + 3.916 = 7.107$, 7.077 (ignition), 7.219, 7.174; average, 7.14×10^{-8} grms. Emanating power = 44.9 per cent. $Ra/U = 3.32 \times 10^{-7}$.

No. 17. Sample of a carload lot (calculated 19 tons) from same locality as No. 13. Per cent U_3O_8 : 3.05, 3.03, 3.06; average, 3.05 = 2.59 per cent U. Average per cent V_2O_5 , 4.66. Ra per grm. $\times 10^8$: 8.66, 8.65 (ignition); average, 8.66×10^{-8} grms. Emanating power = 47.7 per cent. $Ra/U = 3.34 \times 10^{-7}$.

No. 18. Small sample from Kelly Lode No. 3, west of McIntyre District, Colorado, near Utah boundary. Per cent U_3O_8 : 25.63, 25.71; average, 25.67 = 21.77 per cent U. Average per cent V_2O_5 , 22.3. Ra per grm. $\times 10^8$: $1.224 + 6.156 = 7.38$, 7.34, 7.37 (ignition); average, 7.36×10^{-8} grms. Emanating power = 16.6 per cent. $Ra/U = 3.38 \times 10^{-7}$.

No. 19. About 60 lbs. of a composite sample of several ores. Per cent U_3O_8 : 3.18, 3.26, 3.17, 3.10; average, 3.18 = 2.70 per cent U. Average per cent V_2O_5 , 4.03. Ra per grm. $\times 10^8$: (ignition), 8.902, 8.935; average, 8.92 $\times 10^{-8}$ grms. Emanating power = 33.5 per cent. $Ra/U = 3.30 \times 10^{-7}$.

No. 20. A small sample from Horse Mt., Eagle County, Colorado. Per cent U_3O_8 : 7.81, 7.75; average, 7.78 = 6.60 per cent U. Average per cent V_2O_5 , 8.80. Ra per grm. $\times 10^8$: $9.85 + 10.77 = 20.62$, 20.91, 30.63 (ignition), 30.98; average, 30.3×10^{-8} grms. Emanating power = 29.6 per cent. $Ra/U = 4.59 \times 10^{-7}$.

No. 21. A small sample from a Meyer's claim, South Park, Colorado. Per cent U_3O_8 : 9.52, 9.20; average, 9.36 = 7.94 per cent U. Average per cent V_2O_5 , 3.85. Ra per grm. $\times 10^8$: $1.07 + 1.31 = 2.38$, 2.36, 2.37 (ignition); average, 2.37×10^{-8} grms. Emanating power = 45.2 per cent. $Ra/U = 2.99 \times 10^{-7}$.

No. 22. A lot of several hundred pounds from the Wade and Taylor claims, Pac Creek, near Moab, Utah. Per cent U_3O_8 : 7.52 = 6.38 per cent U. Average per cent V_2O_5 , 11.23. Ra per grm. $\times 10^8$: $0.344 + 1.764 = 2.11$, 2.12 (ignition), 2.15; average, 2.13×10^{-8} grms. Emanating power = 16.2 per cent. $Ra/U = 3.34 \times 10^{-7}$.

No. 23. Sample of 1120 lbs. from the same locality as No. 22. Per cent U_3O_8 : 11.62 = 9.86 per cent U. Ra per grm. $\times 10^8$: 3.29, 3.26 (ignition); average, 3.28×10^{-8} grms. Emanating power = 25.1 per cent. $Ra/U = 3.33 \times 10^{-7}$.

No. 24. Sample of about one ton of ore of unknown origin, very finely ground, suspected of being a mill product from which radium had been largely removed, and mixed with a low grade carnotite. Per cent U_3O_8 : 8.83, 8.85; average, 8.84 = 7.50 per cent U. Average per cent V_2O_5 , 6.87. Ra per grm. $\times 10^8$: $3.99, 3.88, 4.24$ (ignition); average, 4.04×10^{-8} grms. $Ra/U = 0.54 \times 10^{-7}$.

(NOTE.—The reasons for distrusting this sample as not being a natural carnotite ore are rather numerous. Its Ra/U ratio is very abnormally low, its origin could not be ascertained. Examined under the microscope it appears full of a net work of crystalline needles partly soluble in water (apparently $CaSO_4$), such as could not have existed in the original ore because the length of the crystals is several times the average diameter of other particles, showing that they must have formed after the ore was ground. On ignition, considerable quantities of sulphur are distilled off, probably owing to reduction of sulphates by organic matter. For these reasons we have not regarded it as natural carnotite, and have presented the data for whatever general interest they may have, without including them in Table IV., however).

TABLE IV.—Summary of Experimental Data for Carnotites.

(All samples starred represent large quantities of ore—several hundred pounds up to 25 tons).

Ore No.	Locality.(a)	U ₃ O ₈ .	U.	Ra × 10 ⁹ per 1 grm. ore.	Eman- ating power. × 10 ⁷ .	Ra/U blende = 100 per cent).	Normal ratio (pitch- blende Per cent.
		Per cent.	Per cent.		Per cent.		
5. Paradox Valley ..	24'25	20'6	49'6	45'8	2'41	72'4	
21. South Park ..	9'36	7'94	23'7	45'2	2'99	89'8	
11. Green River, Utah ..	4'13	3'50	10'95	45'1	3'13	94'0	
3. South of Paradox ..	1'60	1'35	4'26	50'5	3'16	94'9	
8.*South of Paradox ..	4'68	3'97	13'05	33'9	3'29	98'8	
19. (A mixture) ..	3'18	2'70	8'92	33'5	3'30	99'1	
16.*Long Park ..	2'53	2'16	7'14	44'9	3'32	99'7	
14.*Long Park ..	3'93	3'33	11'09	35'2	3'33	100'0	
15.*Long Park ..	2'84	2'41	8'02	43'4	3'33	100'0	
23.*Moab, Utah ..	11'62	9'86	32'8	25'1	3'33	100'0	
13.*Long Park ..	2'78	2'36	7'86	44'7	3'34	100'3	
17.*Long Park ..	3'05	2'59	8'66	47'7	3'34	100'3	
22.*Moab, Utah ..	7'52	6'38	21'3	16'2	3'34	100'3	
18. McIntyre District ..	25'67	21'77	73'6	16'6	3'38	101'5	
1. Long Park ..	2'10	1'78	6'02	29'6	3'38	101'5	
9.*South of Paradox ..	1'52	1'29	4'35	20'4	3'42	102'7	
10.*Paradox Valley ..	2'40	2'04	7'31	29'0	3'58	107'5	
2. Paradox Valley ..	33'22	28'18	101'4	16'2	3'59	107'8	
4. Long Park ..	23'48	19'92	72'8	17'7	3'66	109'9	
7. Long Park ..	3'19	2'70	10'72	39'7	3'97	119'2	
20. Eagle County ..	7'78	6'60	30'3	29'6	4'59	137'8	
Average ..						101'8	

(a) In Colorado when not otherwise specified. See preceding sections for fuller details.

IX. Discussion of Results.

On inspecting the last two columns of Table IV. there appears to be only one possible conclusion as to the radium:uranium ratio of carnotite; namely, that it is identical with that of pitchblende in all large quantities of well-sampled ore. This appears, in general, to be true regardless of the locality or composition of the ore. The low and high ratios occur only in cases of small samples, and are apparently due to local transposition of radium within the ore bed, resulting in differences which are completely equalised on sampling sufficient quantities of ore. We are not prepared to go further into the nature of this transposition at the present time, because, as already stated, the samples were not collected with this object in view.

Of course, the fact that the average of all ratios in Table IV. should be within 2 per cent of normal is somewhat accidental; but the average of all the large samples is within 1 per cent of normal appears by no means accidental, and seems to represent about the average of our limits of experimental error.

The question naturally presents itself as to whether high and low ratios for other minerals can be explained in the same way as for carnotite. As far as the authors are aware, it is true that determinations of the radium:uranium ratio have been made in all the minerals examined on small samples only. On the other hand, it is to be recalled that high ratios had not been hitherto reported except in the case of primary minerals which are not so much subject to the action of water. Furthermore, in the case of autunite, where leaching certainly does produce very low ratios, no high ratios have ever been found to support the view of "transposition" as put forward for carnotite. In such instances it has been found that the leaching process removes the radium completely from association with the original uranium parent, usually disseminating it very widely, or in exceptional cases forming deposits con-

taining considerable radium with no uranium, as found by Jacques Danne in a specimen of pyromorphite at Issy L'Evêque (*Comptes Rendus*, 1905, cxliv., 241).

The difference in the completeness of leaching exhibited by autunite and carnotite may be due to the fact that the latter occurs in a region of very low rainfall; in fact, aridity seems to be a necessary condition for the existence of carnotite. Under such conditions and in view of the fact that the extent of carnotite deposits is frequently quite large, a "transposition" of radium might be expected rather than a complete removal.

The high degree to which carnotite gives up its emanation by diffusion as shown in Table IV. and discussed in Section IV., appears rather remarkable. This property does not seem to be connected with any other known properties of the ores, and we are not able at present to do more than call attention to it, as well as to note that carnotite appears to furnish, in the solid state, a more abundant source of radium emanation than any other mineral with the same radium content.

X. Summary.

1. Samples of carnotite representing large quantities of ore (a few hundred pounds to several tons) show a Ra/U ratio identical with that of pitchblende, $3'33 \times 10^{-7}$.

2. Samples from small quantities (a few pounds) tend to exhibit abnormal Ra/U ratios. One instance as low as $2'48 \times 10^{-7}$ and one as high as $4'6 \times 10^{-7}$ have been found.

3. The most plausible explanation for these ratios seems to be one of "transposition" of radium within an ore bed, producing local differences which are equalised in mixing large quantities of ore.

4. The "emanating power" of carnotite is high, and varies from 16 to 50 per cent.

5. In order to obtain concordant results by the Boltwood emanation method, it was found desirable to determine the emanation liberated by solution in the same sample from which the emanating power had just been determined, thus making the two determinations strictly "complementary."

6. Radium may be more easily determined by the emanation method in one operation either by solution or by ignition from tubes in which it has been sealed for one month to reach equilibrium.

7. In contrast with the successful solution or ignition method for de-emanating carnotite, fusion with carbonate, and also the fusion and solution methods both gave low results and were abandoned.

It gives us great pleasure to acknowledge our indebtedness to Prof. R. B. Moore for his helpful advice during this investigation.

POTASH SALTS.

SUMMARY FOR 1913.*

Compiled by W. C. PHALEN, United States Geological Survey,
Washington, D.C.

(Continued from p. 233).

Investigations by the Bureau of Soils (continued).

With reference to the composition of giant kelps, Merz has found that *Nereocystis* of Alaska waters is, as respects potash content, of as great importance as an economic source of potash salts as that of the more southern waters. *Macrocystis* contains a lower percentage of potassium than does *Nereocystis*, while *Alaria* contains a decidedly lower percentage. The seaweeds *Fucus* and *Porphyra* are evidently valueless as sources of potash on an economic scale.

Another observation made in connection with Merz's work is that in every instance where stems and leaves were

* From *The Chemical Engineer*, xx., No. 3.

separately analysed the total salt content, and similarly the potash content, in the stem exceeded that in the leaves, a conclusion at variance with that previously but tentatively drawn by Cameron. It was also found that (1) the ash content is generally higher in the leaves than in the stem of the same plant, and (2) that the nitrogen content is generally larger in the laminae than in the stipe of the same plant.

The work of Parker and Lindemuth (*Journ. Ind. and Eng. Chem.*, v., p. 287, April, 1913) on the giant kelps has enabled them to draw the following conclusions. These kelps are the most important from an economic point of view, both from their size and from the large amount of potash salts which they contain. They occur from 30 to 200 feet in length, and in specific cases much longer, while the smaller varieties occur only from 2 to 12 feet in length. In the northern areas the commercial species are *Nereocystis leutkeana* and *Macrocystis pyrifera*, in the southern areas the commercial species are *Macrocystis pyrifera* and *Pelagophycus porus*. Other conclusions which these workers have been able to draw from their experiments are (1) that the average content in potassium chloride in the giant kelp is high; (2) that apparently no definite relation exists between the different constituents of kelp; (3) that apparently the northern kelps are richer in potassium chloride than the southern; (4) that the potash content of *Nereocystis* is greater than that of *Macrocystis*; and (5) that the iodine content of the northern and southern kelps shows no conclusive differences.

In a paper by F. K. Cameron (*Franklin Inst. Journ.*, clxxvi., p. 347, October, 1913) on kelp and other sources of potash, the recent information regarding kelp as a source of potash is summarised up to the time of publication. From the averages of the many existing analytical data Cameron states the following conclusions, derived in part at least from the work of his colleagues of the Bureau of Soils: (1) No definite quantitative relations exist between the different constituents of kelp; (2) the potassium content of *Nereocystis* is greater than that of *Macrocystis*; (3) the potassium content of northern kelp is higher than that of southern kelp; and (4) there is no positive difference in iodine content between northern and southern kelps. So far as results obtained are available, Cameron considers that the following conclusions also seem justified: (5) The proximity of the mouth of a fresh-water stream has no appreciable effect on the potash and nitrogen content of kelp; (6) there are no essential differences between the potash and nitrogen content of fronds and stipes (which conclusion was changed by the subsequent work of Merz, already referred to); and (7) there are no essential differences in the potash and nitrogen content of old and young plants, but further data on this point are desirable, as well as on the possible variations in the potash content with the season.

Commercial Utilisation of Kelp.

Since interest has been aroused in kelp as a source of potash salts, several companies have been formed having in view its commercial exploitation either in the dried form as a fertiliser or for the potash salts and the other valuable ingredients, such as iodine, which it contains. The names of eleven companies, formed ostensibly to engage in the kelp industry, have been brought to the attention of the Survey during the last year. In geographical distribution these companies are located in the vicinity of Puget Sound, with headquarters chiefly at Seattle, and on the Southern California coast near Long Beach, Los Angeles, and San Diego. Two of these companies were mentioned in this report for 1912.

The American Potash Co., with offices at Los Angeles, Cal., plans to utilise the kelp in the vicinity of Long Beach. This company was formed by the merging of two other companies, one of which was the Coronado Chemical Co., of San Diego and Cardiff. It is stated that work will begin early in 1914 on the manufacture of potash and other

by-products from kelp at a plant to be built at Long Beach. The plant is to be erected on the unit system, and construction work on it began early in 1913. The work of manufacturing potash will begin on the completion of the new buildings, that are expected to be finished about April 1, 1914.

The Pacific Products Co., of San Pedro, Cal., with a capital of 100,000 dol., is reported to have a factory site on the California coast, opposite the kelp grove outside of Point Firmin.

The Pacific Products Co., of Seattle, Wash., capitalised at 125,000 dol., will build a factory for the manufacture of fertiliser materials and by-products from fish and kelp at Port Townsend, Wash. Several beds of kelp have been optioned at the head of Puget Sound, where a large quantity of seaweed will be harvested each year and transferred to the factory at Port Townsend. This company will also make a business of obtaining dog-fish and of utilising the offal from the fish canneries in the vicinity. The first unit of the plant for converting kelp and dog-fish into fertiliser material was reported completed in July, 1913.

The Pacific Kelp Mulch Co. is located at Terminal Island, one mile east of East San Pedro, on the San Pedro, Los Angeles, and Salt Lake Railroad. The company has been gathering kelp from the ocean during the last two years and disposing of it to the farmers and fruit growers as a fertiliser. The company has developed a machine which harvests the kelp rapidly and on a large scale. The kelp is cut from 4 to 6 feet under water, and care is taken not to disturb the roots of the growing plants. It is loaded on a barge and brought to the boat landing of the plant. Here it is pitchforked from the barge on a belt conveyer, which conveys it to the cutter, being subjected during the passage to a steaming process, which is practically instantaneous, and which, it is asserted, removes all the adhering common salt (NaCl) but none of the potash salts. The cutter chops it into pieces 6 to 8 inches long—that is, of a length to be conveniently handled with a manure fork, or to be harrowed under the soil after being spread. From the cutter the kelp falls into wagons or to the floor. It is then carted to the railroad and dumped into freight cars, and shipped to the centres of consumption. This company has the distinction of being the first to harvest and market kelp on a commercial scale.

The material is said to have many advantages as a fertiliser, and these are explained in a small pamphlet which has been issued by the company.

The other companies whose names have come to the Survey as proposing to engage in the production of kelp on a commercial scale are the following:—

Ocean Products Co., Seattle, Wash.
North Pacific Kelp Potash Co., Seattle, Wash.
Pacific Coast Kelp Potash Co., Seattle, Wash.
Puget Sound Kelp Potash Co., Seattle, Wash.
Aquatic Products Co., Seattle, Wash.
Kelp Products Co., San Francisco, Cal.
Mexican Kelp Fertiliser Co., Los Angeles, Cal.

The Survey has no first-hand knowledge of the activities of these companies.

Alunite and Kelp as Fertilisers.

In experiments with alunite as a source of potash, Waggaman (*Circular* 70, U.S. Dept. Agr., Bureau of Soils, July 31, 1912) found that a large quantity of water is required to free the ignited residue entirely from soluble salts, and that the subsequent evaporation is tedious and expensive. He suggested, therefore, that it might be more economical to use ignited alunite directly as a fertiliser than first to leach the residue for the potassium sulphate contained in it.

Experiments have been made by Skinner and Jackson ("Alunite and Kelp as Potash Fertilisers," *Circular* 76, U.S. Dept. Agr., Bureau of Soils, April 10, 1913) with alunite as a fertiliser in which both the raw and the ignited

mineral have been used. The sample of raw alunite containing 10 per cent potash (K_2O) was finely ground, as was also the sample of the ignited mineral which contained 14.7 per cent potash. These minerals were applied to the soil in such quantities as would furnish 25, 50, 100, 200, and 500 lbs. of potash to the acre. Experiments with kelp were also tried, the material used being in the dried state and containing 19.8 per cent potash. This likewise was applied to the soil in such quantities as to furnish 25, 50, 100, 200, and 500 lbs. of potash per acre. Check experiments were also made containing equivalent quantities of potash in the forms of the sulphate and the chloride, while in still another experiment no fertiliser was used. This last was in the nature of a control experiment.

The cultural methods employed and the results obtained from these experiments are as follows:—

The soil was weighed into pans, 3 lbs. to each pan. The soil in one pan received no fertiliser and was used as a control. To each of the other pans the fertiliser to be tested was added. To the different pans of soil were added raw alunite, ignited alunite, kelp, potassium sulphate, and potassium chloride, each in quantities of 25, 50, 100, 200, and 500 lbs. of potash (K_2) per acre, based on an acre half-foot of soil weighing 2,000,000 lbs.

Effect of Alunite and Kelp as Compared with that of Potassium Sulphate and Potassium Chloride on Growth.

Treatment.	Quantity of K_2O added per acre. Pounds.	Green weight. Grms.	Relative growth. Per cent.
Soil untreated	—	3'35	100
Soil + raw alunite ..	25	3'70	110
	50	4'00	119
	100	4'02	120
	200	3'77	112
	500	3'72	111
			114
Soil + ignited alunite	25	4'58	136
	50	4'77	142
	100	4'80	143
	200	4'80	143
	500	4'53	135
			140
Soil + kelp	25	3'93	117
	50	4'67	139
	100	4'80	143
	200	4'40	131
	500	4'30	128
			131
Soil + K_2SO_4	25	4'27	127
	50	4'33	129
	100	5'12	152
	200	4'52	135
	500	4'90	146
			138
Soil + KCl	25	4'40	131
	50	4'33	129
	100	4'50	134
	200	4'37	130
	500	4'40	131
			131

by sifting, and was potted October 28. Three pots, each holding about a pound of soil, were used for each treatment. Six wheat plants were planted in each pot. The plants grew until November 29. At the end of the experiment the plants were cut and the green weights recorded. The results of the test are given in the accompanying table. The last column gives the relative growth of the different treatments. The growth of the check or control is taken as 100. The second column gives the green weights of the three cultures in each treatment.

By examination of the table it is seen that each of the potash fertilisers produced an increased growth over the untreated soil. The raw alunite used in amounts of 25 to 500 lbs. of K_2O per acre increased growth from 10 to 20 per cent. The best results were secured with 50 to 100 lbs. of potash (K_2O) per acre. The average increase over the untreated soil of the five amounts was 14 per cent. When the growth is compared with that produced by the ignited alunite it is seen that this caused larger growth with each amount used than did the raw alunite. The increase in growth with ignited alunite over the untreated soil varied from 35 to 43 per cent, the average increase being 40 per cent. The growth with the raw alunite was not so good as with similar amounts of potash as potassium sulphate and potassium chloride. The average increase with potassium sulphate was 38 per cent, and with potassium chloride was 31 per cent. The effect of ignited alunite was about the same as that of potassium sulphate and greater than that of the potassium chloride.

Effect of Alunite and Kelp as Compared with that of Potassium Sulphate and Potassium Chloride on Growth.

Treatment.	Quantity of K_2O added per acre. Pounds.	Green weight. Grms.	Relative growth. Per cent.
Soil untreated	—	2'84	100
Soil + raw alunite ..	25	3'35	118
	50	3'40	120
	100	3'36	118
	200	3'36	118
	500	3'02	106
			116
Soil + ignited alunite	25	3'54	124
	50	3'70	130
	100	3'70	130
	200	3'90	137
	500	3'94	136
			131
Soil + kelp	25	3'24	114
	50	3'54	124
	100	3'59	127
	200	3'60	127
	500	3'45	121
			123
Soil + K_2SO_4	25	3'08	108
	50	3'62	127
	100	3'87	136
	200	3'68	129
	500	3'54	124
			125
Soil + KCl	25	3'04	108
	50	3'50	123
	100	3'50	123
	200	3'74	131
	500	3'60	127
			122

The soil used in the first experiment was the Carrington loam—a soil which is known to respond well to potash fertilisers in field practice. The soil was treated with the various fertilisers in pans on October 22, was well mixed

Kelp produced a considerable increase in growth over the untreated soil. The increase varied with the different amounts, from 17 to 43 per cent. The average increase over the untreated soil was 31 per cent. The increased growth was about the same as that produced by potassium chloride, and was slightly less than that resulting from the use of potassium sulphate. It should be here noted that the potash in the kelp is in the form of the chloride.

Another experiment was made to test the effect of these potash compounds, using this time a different soil. Otherwise the details of the experiment were the same as in the first test. The soil used in this test was the Volusia silt loam. The plants grew from November 19 to December 21. Three pots were used for each treatment. The results are given in the accompanying table (see preceding column).

Each of these potash fertilisers had a beneficial effect on Volusia silt loam. The raw alunite again produced less increased growth than the ignited alunite. This was true with each amount of the substances used. The raw alunite was not as effective as potassium sulphate and potassium chloride. However, the ignited alunite was more effective. The average for the raw alunite was 16 per cent, for the ignited alunite 31 per cent, for potassium sulphate 25 per cent, and for potassium chloride 22 per cent.

As in the first experiment, kelp again produced considerable increase in growth. The effectiveness in producing plant growth was practically the same as that of potassium sulphate and potassium chloride. Kelp gave as an average 23 per cent increase in growth, potassium sulphate 25 per cent, and potassium chloride 22 per cent increase. In addition to the amount of potash added to the soil by the kelp, it contains a small amount of nitrogen and phosphorus, which should be effective in the soil. From these two experiments it seems that the dried kelp and ignited alunite are about as effective potash fertilisers as the salts, potassium sulphate and potassium chloride.

(To be continued).

REPORT OF THE EMERGENCY COMMITTEE ON COMPETITION WITH GERMAN AND AUSTRIAN TRADE.

THE Manufacturers' Section of the London Chamber of Commerce recently appointed a committee to enquire into the question of the extension of the business of British manufacturers and merchants in the United Kingdom, the Colonies, and foreign countries. The Committee issued two sets of questions, inviting merchants and manufacturers to reply to them, and has now published an analysis of the replies received. Manufacturers were asked whether they were prepared to undertake the production of goods other than those with which they had previously been mainly concerned, and were also asked whether they had been importing any of their raw materials from Germany and Austria, and whether they wished to be informed of alternative sources of supply. Merchants were asked whether they had in the past been in the habit of procuring goods from Germany or Austria, and whether they would be willing to give a preference to British made goods. Other questions of a similar nature were also put, and suggestions and observations were invited. From the replies obtained lists of goods which merchants are requiring to replace German or Austrian goods were compiled, and many manufacturers stated that they were willing to manufacture various articles other than their usual lines, in order to keep their workpeople employed. Lists of these goods will be found in the *Chamber of Commerce Journal* for October, 1914, and further information with the names and addresses of the firms in question may be obtained from the Statistical

and Information Department of the London Chamber of Commerce, 97, Cannon Street, London, E.C.

The communications received by the Chamber show that there is no disposition to undertake the manufacture of goods requiring expensive plant or special machinery, but that many manufacturers are quite willing to keep their workpeople employed by producing small articles which can be made without much technical skill or expensive machinery. It is suggested that a scheme should be instituted by the Government to assist firms having large uncollectable assets due from foreign countries, and that measures should be taken as soon as possible to re-establish foreign exchange operations on a satisfactory basis.

The chief feature of the present situation is the need for adequate capital, while manufacturers also demand some assurance on the part of the Government that they will be enabled after the war to carry on freshly established industries in face of foreign competition. It is suggested that code telegraphic facilities should again be permitted, and that the excise duties on alcohol, &c., should be relaxed when the spirit is to be used for industrial purposes. The allotment of Army contracts should not be confined within the present comparatively narrow limits, and the existing Factory Acts should be amended to allow for more elastic hours and conditions as to working arrangements.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 23, 1914.

Prof. Sir J. J. THOMSON, O.M., F.R.S., President,
in the Chair.

THE following is an abstract of the Presidential Address delivered by Prof. THOMSON, the subject being "Ionisation":—

Ionisation is the process by which ions—particles charged with electricity—are produced in a solid, liquid, or gas. This address is confined to the consideration of ions in gases, and deals with two questions—(1) the nature of the ions, (2) the process by which they are produced. The evidence as to the nature of ions is derived from experiments on their mobility, which have shown:—

a. The mobility of a positive ion depends only on the gas through which the ions are moving, and not on the nature of the gas out of which the ions are formed.

β. The mobility of the ions in a gas at constant density is independent of the temperature.

γ. There are a considerable number of gases in which the mobility is very approximately inversely proportional to the square root of the density of the gas.

δ. In the case of negative ions there is an abnormal increase of mobility when the pressure is reduced below a certain value, and there is some evidence that this is also the case for positive ions at very low pressures.

Two theories of the mobilities of ions were considered, one founded on the view that the action between ions and molecules is analogous to impacts between hard elastic spheres, the other on Maxwell's theory of forces between ions and molecules varying inversely as the fifth power of the distance between them.

It is shown that *a* follows from the second theory, provided the ion is a cluster whose mass is considerably greater than that of a molecule of the gas through which it is moving. On this supposition it follows, also, from the first theory, if we suppose, in addition, that all ions in a given gas are of the same size.

(8) follows at once from the second theory; to explain it on the first theory we must suppose that the size of the

ion varies with the temperature in a definite way. The necessary relation can be deduced from thermodynamical principles if we suppose that the force between an ion and a molecule is analogous to that between a charged point and a sphere which is either a conductor of electricity or has a high specific inductive capacity.

(γ) requires on theory one that the ions in these gases should be of the same size; on theory two, that the molecules of these gases should exert the same force on a charged point at a given distance.

(δ) follows on either theory if the ion dissociates at low pressures so that free corpuscles are present in the gas.

With regard to the process of ionisation, the first stage of this in the vast majority of cases consists in the detachment of an electron or corpuscle. Evidence as to the method by which this takes place is afforded by determinations of the velocity with which the electrons are ejected from the body.

In the case of ionisation by light or Röntgen rays, this velocity depends primarily on the wave-length of the radiation, not upon its intensity, nor, at any rate to any great extent, on the nature of the molecule from which the corpuscle is ejected. This velocity is far greater, even when every allowance is made for resonance, than can be accounted for if we suppose that the energy of the light is uniformly distributed, and that the corpuscle acquires its velocity by the action on it of the electric force in the wave. Another explanation not open to these objections was put forward.

When ionisation is due to the action of moving electrified particles, whether positive or negative, the results are quite different. The velocity of the ejected particles (δ-rays, as they are sometimes called) does not seem to vary much, if at all, with the velocity of the particles which eject them, and is of the same order whether these particles are positive rays or the much swifter cathode rays. The method of ejection by the impact of such particles was considered, and suggestions as to a possible theory and some of its consequences thrown out.

Dr. R. T. GLAZEBROOK, in moving a vote of thanks to the President, said that one expected when listening to Sir J. J. Thomson to be carried to the bounds of knowledge by one who had taken no small part in the extension of these bounds, and he was confident that none of those present had been disappointed in that expectation. He asked the President, on behalf of the Society, to allow his address to be published in full in the *Proceedings*.

Dr. C. CHREE seconded the vote of thanks, which was carried with enthusiasm.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, November 4, 1914.

Mr. A. CHASTON CHAPMAN, President, in the chair.

Messrs. William Roscoe Hardwick, Harold Fletcher Hills, and Robert Hindle Kay were elected members of the Society.

Certificates were read for the first time in favour of Messrs. Harold Stanley Machin, Cleve, Oaklands Park, Weybridge, Surrey; and Frederick Robinson, The Hollies, Mile End, Stockport, Cheshire.

Certificates were read for the second time in favour of Messrs. John Kent Crow and Horace Finnemore.

The following papers were read:—

"Notes on Bleached and Unbleached Flour." By R. T. THOMSON.

This paper gives the results of certain observations made in the examination of bleached and unbleached flour, dealing with "Acidity," which is shown to be a mere assumption; certain effects of bleaching with nitrogen peroxide; also some tests showing the proportion of sulphates and lime in wheat products.

"Methyl Red as Indicator." By R. T. THOMSON.

The object of this paper is to "place" methyl red in its proper position as an indicator for acids and alkalis. Recent notices would appear to class it along with methyl orange in its properties, but the author gives results showing its affinity to litmus.

"Notes on Vinegar." By J. S. JAMIESON.

The author compared the composition of a vinegar prepared from malted maize before and after pasteurisation with ordinary barley-malt vinegar, and found that the figures for nitrogen and phosphoric acid for the maize vinegar are much lower, and the extract and total solids higher than in genuine malt (barley) vinegar. He concludes that the proteins and phosphates are not so readily extracted by an aqueous infusion from malted maize as from malted barley.

"Two Rapid Methods of Estimating Water in Crude Petroleum, Oil Fuel, and similar substances." By HERBERT S. SHREWSBURY.

Two new methods are described. The first, a distillation method, is conducted in a new form of apparatus, in which condenser and receiver are one and the same vessel. A 500 cc. distillation flask containing 100 cc. (or the volume equivalent to 100 grms.) of the sample and some dry pumice, is arranged with its side tube at right angles to the bench, and inserted to the neck in a graduated cylinder of slightly greater bore. The cylinder may be 50 cc. capacity or larger if necessary, and should be graduated in tenths per cent. It is supported in a vessel with an outflow at its base, through which water is passed from the tap at a sufficient rate to keep the vessel full. The flask is heated with a naked Bunsen flame, the burner being held in the hand, and the flame passed continually over the whole surface of the glass, commencing from the cork, great care being taken to keep the glass portions uncovered by the oil at a high enough temperature to prevent condensation of water. If water drops roll into the hot oil, violent bumping ensues. Finally, several cc. of the dried oil are distilled, and the water measured after addition of dry petroleum ether and vigorous rotation and a sufficient period of standing.

In the second method, 10 cc. of glacial acetic acid in a dry stoppered 25 cc. cylinder are mixed with 10 cc. of oil fuel, shaken, and transferred to a dry separator. The acid extract is separated and filtered, and 2 cc. are mixed with 2 cc. of the standard oil (equal volumes of arachis and coconut oils were found satisfactory in the Tropics) in a dry test-tube, heated till clear over a spirit flame (the low temperature of which is more convenient than that of a Bunsen burner), and the turbidity temperature observed in the usual way by stirring with a thermometer. A blank is made in the same way on 10 cc. of the oil dried by heating in an open dish. The turbidity temperature obtained, minus that of the glacial acetic acid used, yields the blank, which is subtracted from the turbidity temperature obtained from the wet oil. The final temperature is compared with those obtained from standards differing by tenths per cent from 0—2.6, prepared by adding the necessary proportions of water to the glacial acetic acid used. For higher percentages than 2.5 the extracts for determination and blank must be diluted with the same quantities of glacial acetic acid and the percentages obtained multiplied by the ratio of dilution. Every fresh stock of acetic acid must be standardised in this way, and the mean increase of turbidity temperature per 0.1 per cent water is 2.2° C.; blanks are about 9° C. When standards are prepared a determination may be completed under ten minutes. The same blank may be used for sufficiently similar oils. The methods agree well in their results, the differences obtained on five samples ranging from nil to 0.15 per cent of water. Two prepared samples, containing respectively 1 and 10 per cent of water, yielded 1.00:1.30 and 9.70:10.00 respectively by the distillation and turbidity temperature methods. The methods are probably applicable to oils and fats generally.

NOTICES OF BOOKS.

Dairy Chemistry. By HENRY DROOP RICHMOND, F.I.C. Second Edition. London: Charles Griffin and Co., Ltd. 1914.

THE chemical control of dairy work is admirably treated in this book, the second edition of which has been considerably enlarged and improved by the addition of descriptions of recent analytical methods and of new processes. The chemical properties of the constituents of milk are given in detail, and the best methods of analysing milk and dairy products are carefully described. The analysis of water and its bacteriological examination are included. The discussion of some typical problems which the dairy chemist may be called upon to solve will be found very useful, and both from a theoretical and practical point of view the book is a valuable addition to the literature of analytical chemistry.

Essays and Addresses. By the late JAMES CAMPBELL BROWN, D.Sc. (Lond.), LL.D. (Abdn.). London: J. and A. Churchill. 1914.

THIS collection of addresses and lectures delivered by the late Dr. Campbell Brown provides some excellent illustrations of his characteristic style. The subjects dealt with include technical education, upon which very decided views are expressed, and the choice of chemistry as a profession. Some biographical addresses are also included, a sketch being given of the work of Justus von Liebig, prepared from some notes compiled by himself, and also some interesting reminiscences of Hofmann and the early days of the College of Chemistry. In a lecture on a French view of German industries Dr. Campbell Brown discussed the secret of the wonderful success of Germany from an industrial point of view, basing his remarks upon an article which appeared in the *Revue des Deux Mondes* in February, 1898. The lecturer was clearly a man of wide reading and liberal views, with a keen sense of humour, and a remarkable power of making his subject interesting, and imparting precise information in a very acceptable form.

Filters and Filter Presses for the Separation of Liquids and Solids. From the German of F. A. Bühler, with Additional Matter by JOHN JOSEPH EASTICK, F.I.C., A.R.S.M. London: Norman Rodger. 1914.

IN the translation of this book from the German many important additions have been made. It was thought advisable that the processes of filtration employed in one important industry should be described in full, and the sugar industry was selected as being the most suitable on account of the great variety of filters employed. Some account has also been added of the theory of filtration, and British patents have been substituted for German, thus greatly adding to the value of the book for English readers. The descriptions of different types of filtering apparatus are in all cases detailed, and are fully illustrated by diagrams, which occupy a large proportion of almost every page.

Gases Found in Coal Mines. By GEORGE A. BURRELL and FRANK M. SEIBERT. Washington: Government Printing Office. 1914.

THIS pamphlet is intended for the use of the miner who wishes to know something about the dangers which attend him in his daily work, and thus be in a position to protect himself and his fellow-workers. A short simply-worded account is given of the composition of normal air and of the elementary properties of the gases constituting it. The changes it undergoes after entering the mine are explained, and the properties of the dangerous gases or damps are described fully. A very clear summary is provided of the warnings given by flames, &c., in different circumstances, and practical suggestions are made as to the precautions which should be taken to avoid accidents.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Atti della Reale Accademia dei Lincei.
Vol. xxiii. [ii.], No. 1, 1914.

Polysulphides of Calcium.—G. A. Barbieri.—The supposed polysulphides of calcium have not yet been isolated in the solid crystalline state. From solutions of them basic salts of uncertain composition crystallise, and the existence of the tetra- and penta-sulphide has not yet been definitely established. The author has applied his method of the fixation of the labile hydrated salts by means of hexamethylene tetramine to the study of these polysulphides. By the double decomposition in solution of ammonium pentasulphide and calcium chloride in presence of hexamethylene tetramine, yellow crystalline prisms of $\text{CaS}_5 \cdot 10\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$ are obtained, while the corresponding compound of CaS_4 is prepared by using ammonium polysulphide solution which is less rich in sulphur. It can thus be shown that the yellow solution obtained by boiling sulphur with milk of lime contains calcium tetrasulphide, while the pentasulphide is present in the solution obtained by saturating a solution of calcium sulphhydrate with sulphur.

Isomorphism of Perchlorates and Permanganates.—G. Scagliarini and A. Marangoni.—In the course of the study of the isomorphism of perchlorates and permanganates the authors have prepared ammoniacal silver perchlorate, $\text{AgClO}_4 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$, by adding a pure concentrated solution of sodium perchlorate to a concentrated ammoniacal solution of silver nitrate. The salt separates in needle-shaped crystals. The permanganate, $\text{AgMnO}_4 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$, can be prepared similarly. A permanganate of magnesium or nickel and hexamethylene tetramine can be obtained by adding a concentrated solution of potassium permanganate to a pure concentrated solution of magnesium or nickel acetate and hexamethylene tetramine.

MISCELLANEOUS.

Faraday Society.—A General Discussion on "The Hardening of Metals" will take place on Monday, November 23, at the Chemical Society, Burlington House, London, W. The President (Sir Robert Hadfield, F.R.S.) will preside over the discussion, and among those who will take part therein are Prof. Ernest Cohen (of Utrecht), Dr. G. T. Beilby, F.R.S., Prof. J. O. Arnold, Prof. H. C. H. Carpenter, Dr. C. H. Desch, Prof. C. A. Edwards, Mr. H. L. Heathcote, Mr. J. C. W. Humfrey, Dr. T. M. Lowry, F.R.S., Mr. Andrew McCance, Dr. W. Rosenhain, F.R.S., and others.

MEETINGS FOR THE WEEK.

TUESDAY, 17th.—Biochemical Society, 5.30. (In the Physiological Department, King's College, London).

THURSDAY, 19th.—Royal Society. "The Circulation of the Atmosphere," by A. Mallock. "Origin of the Indo-Gangetic Trough, commonly called the Himalayan Foredeep," by Col. Sir Sidney Burrard. "Approximately Permanent Electronic Orbits and the Origin of Spectral Series," by G. W. Walker. "Spectroscopic Investigations in connection with the Active Modification of Nitrogen—IV. A Band Spectrum of Boron Nitride," by W. Jervons. "Additional Note on the Production of High Permeability in Iron," by E. Wilson.

Chemical, 8.30. "Dissociation Pressures of the Alkali Bicarbonates—Part II., Potassium, Rubidium, and Caesium Hydrogen Carbonates," by R. M. Caven and H. J. S. Sand. "Studies in the Camphane Series—Part XXXVI., N-Chloro-aminocamphor," by M. O. Forster and M. Schlaepfer. "Experiments on the Removal of Sulphur from Silver," by C. C. Bissett.

THE CHEMICAL NEWS.

VOL. CX., No. 2869.

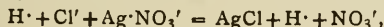
THE SYMBOLICAL REPRESENTATION OF ANALYTICAL OPERATIONS.

By L. GOWING-SCOPES.

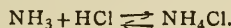
If we wish to represent a chemical reaction by means of symbols we can write the chemical equation of the reaction. For instance.—



and at a glance we can see exactly what has happened, what the products are, and how they are formed. We can even go further and write the reaction as follows:—



which gives an even fuller insight into the mechanism of the reaction. We also have a scheme for showing how a reaction goes when it can take place in either direction of the equation according to the conditions under which the experiment is made—the so-called “reversible” reactions. For example:—



Here we have introduced a new symbol to indicate that under certain conditions ammonia and hydrochloric acid combine to form ammonium chloride, while under other conditions ammonium chloride gives ammonia and hydrochloric acid.

If, however, we wish to express by means of symbols in a condensed manner, how the experiment is to be conducted, under what conditions of temperature, time, &c., we cannot at present do it, and we have to be satisfied with either an oral or written description.

Under certain conditions both these methods present disadvantages for the description of analytical operations. The written or printed description is very tedious to go through when one is searching the literature of various analytical processes, and much time and trouble would be saved if all such descriptions were followed by a condensed version in symbols which could be instantly comprehended. Likewise when one is listening to a paper being read it is often difficult to follow the experimental details of a process, particularly when such description is read rapidly and not illustrated by diagrams or experiments. A condensed symbolical version written on the blackboard would here, again, be invaluable.

The present communication is an attempt to overcome some of these difficulties.

All analytical operations involve the question of temperature and time. In many cases these are not definitely expressed, but are left to the judgment of the analyst. In most cases, too, the question of weight and volume is involved, likewise the use of reagents.

Some thirty or forty operations are very common, and one comes across one or another of them in every line of a description of a method of analysis. These and some less common operations may be all represented by symbols to be described later. For the present, let us take, say, the letter P to indicate some analytical operation. Now P may have to be performed at some definite temperature—say, 100—and we may write—



which we instantly read as operation P to be performed at 100° C. The operation may have to last some definite time—say, five hours—we can then write—



which we read as operations P performed at 100° C. for five hours. The use of a reagent may be involved, when we can write—



which reads as operation P performed at 100, and for five hours after application or use of reagent (HCl).

Symbols may be modified by such operations as shaking, stirring, &c. These may be indicated by using various kinds, of lines to underline symbol. For instance, we can write—



which may be taken to mean operation P is performed at 100° C. for five hours after use of HCl, the operation being performed very carefully (indicated by line under symbol). Furthermore, the symbols may be turned upside down, made thick or thin, &c., to indicate some new operation.

Working on these lines it was found possible to draw up the following rules for writing symbols:—

- (1) A symbol may be turned upside down to mean exactly opposite to what it means the right way up, but it may be placed in other positions to mean operations relating to the operation understood when symbol is right way up.
- (2) All existing symbols to bear their usual meaning.
- (3) When the symbol is indicated by two letters the symbol may be read if applicable as “large” or “small” according as to whether the second letter is large or small.
- (4) All symbols to be made so that their appearance at once brings to mind their meaning.
- (5) Each symbol to be divided from the next by a perpendicular line. A double perpendicular line indicating the beginning and ending of the analysis.

Rules for Writing Symbolical Operations.

1. The symbol of the operation to be written first of such a size as to take up about one-third of the total height of the symbolical expression.
2. Temperatures and temperatures only are to be written above symbol. To be written in very small characters, and to be always understood to indicate °C. unless otherwise stated.
3. Time and time only to be written below symbol. To be written in very small characters, and all figures to be followed by “h” or “m” to indicate either hours or minutes.
4. Lines modifying symbols, such as shake, &c., to be placed immediately below or above symbol coming between symbol and figures indicating time or temperature.
5. All figures in *light* type to represent weight in grms., and all figures in *heavy* type to represent volume in cc.
6. Reagents to be indicated by their formula or contraction, the one on left of symbol to be read first. Formula or contractions in *light* type indicates cold reagent. Formula or contractions in *heavy* type indicate hot reagents. Dilute reagents to be written in italics. All reagents to be written in as small type as possible, and must not occupy more than two lines on either side of symbol, the total height of the two lines and spaces not to be more than average height of symbols. When two lines exist the top to be read first.
7. Written matter in small type may be inserted for an uncommon operation for which no symbol exists, but total height of lines and spaces not to be more than total height of a symbolical expression.

The accompanying symbols have been devised, and in many cases are ordinary letters of different shapes used in various positions.

Take or weigh out in grms.	[3]		
Take in cc.	[3]		
Filter, keep precipitate and filtrate	<		
Filter, reject filtrate	∇		
Filter, reject precipitate	∧		
Remove precipitate from filter	>v		
Filtrate	v		
Wash with ——— till free from ———	$\frac{PQ}{W}HQ$		
Wash by decantation	W		
Heat.	H		
Heat till dissolved	H _{MA}		
Heat to boiling	H _B		
Heat to fusion. Fuse	H _F		
Warm	h		
Cool	y		
Ignite	I		
Evaporate to dryness	D _D		
Evaporate to small bulk	D		
Evaporate to — cc.	D _s		
Evaporate off alcohol	D _{AL}		
Dilute to — cc.	D ₁₀₀		
Acidify	A		
Make alkaline.	∇		
Make neutral	∧		
Dry	D		
Dry to constant weight.	D _{GW}		
Large excess	EX		
Small excess	Ex		
Powder coarsely	PD		
		Powder finely	P _D
		Treat with or add.	—
		Digest with	D→
		Treat with till faint permanent precipitate forms	→
		Moisten with.	H→
		Dissolve	I
		Precipitate	↓
		Pass in gas	↘
		Remove gas	↗
		Allow to settle	↓
		Decant	↓
		Transfer	X
		Reduce with	∇
		Oxidise with	∧
		Small quantity	p
		Large quantity	P
		Distil	S
		Distillate.	↘
		Allow to stand	S
		Mix (with)	X
		A few drops	:
		7 drops	7.
		Extract (with)	Q
		Weigh as	BA ₅₀ Q
		Titrate with n/x HCl, using methyl-orange as indicator	T _{MO}
		Electrolyse	+ -
		Shake well	~
		Stir	—
		Perform operation as rapidly as possible.	—
		Perform operation very carefully	—

Determine melting-point	MP.
Determine boiling-point	BP.
Determine freezing-point	FP.
Determine molecular weight	MW _T
Determine viscosity. Time of efflux	V _{IS}
Determine refractive index.. .. .	N _D
Determine sp. gr. compared with water at — ..	$\frac{D_4^{20}}{D_4^{20}}$
Polarise	—
Charge	Δ
Slag.. .. .	S _{LAG}
Pour in mould	↓
Button	○
Cupel	☐
Flask	🍷
Condenser (reflux)	🌀
Condenser (distilling)	🌀
Water oven	☐
Air oven	☐
Evaporating basin.. .. .	☐
Watch-glass (cover with)	☐
Beaker	☐
Bunsen burner	🔥
Muffle	🔥
Furnace	🔥
Water-bath	🔥
Burette	📏
Pipette	📏
Crucible	🔥
Anode	—
Cathode	+

Referring to the table, square brackets may always be taken to mean "Take," "Weigh out," or "Measure out" the quantity contained by them.

The symbols relating to filtration are represented by a thin "V." This was chosen, as it brings to mind a folded filter-paper.

With regard to the washing of precipitates no simple symbol calling to mind the operation could be thought of, so in this case the first letter was chosen. The liquid used for washing is placed on the left and the substance to be washed out on the right.

Again, with the section on "Heat" the first letter has again been employed. "Till dissolved" is distinctly a matter of time, therefore "DIS" is placed under the symbol in the line reserved for time. "Boiling" and "fusion" are clearly temperatures, therefore "B" and "F" are placed above symbols in the temperature line.

The operations relating to evaporation may conveniently be represented by a thin elongated "D," which on its back resembles an evaporating basin. By turning this symbol upside down the reverse operation to evaporation, *i.e.*, dilution, is obtained.

With reference to the symbol for "Dry to constant weight," "constant weight" is clearly a function of time, and we can put "c.w." under the symbol in the time line.

Excess is an example where the size of the second letter determines whether it shall be "large" or "small."

The symbol for "treat with or add" is the only symbol used, already in existence in general use; it was a development in the use of this symbol that led to the idea of the present communication.

Passing on we come to "oxidise" and "reduce": these can easily be remembered according as the substance under treatment increases or decreases in mass.

"Small quantity" and "Large quantity" were derived from a pile of substance on the end of a spatula.

The symbol for "weigh as" is derived from the shape of the balance beam.

"Electrolyse" is obtained by the recognised symbols for the two electrodes.

Shake well is remembered by the up and down motion.

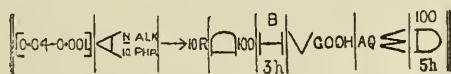
Stir is remembered by the rather irregular performance of this operation.

Determine specific gravity is of course derived from the Sprengel tube. The temperature at which it is to be taken is placed on the right, and the temperature at which it is to be compared with water on the left.

The symbols for apparatus explain themselves.

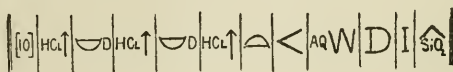
Examples in Use of Symbols.

Estimation of Citric Acid.—A quantity of the substance, not more than 0.04 grm. and not less than 0.001 grm., is exactly neutralised with N/10 alkali, using phenolphthalein as indicator. Ten cc. of reagent are added, and the whole diluted to 200 cc. The mixture is boiled for three hours, filtered through a Gooch crucible. The precipitate is first washed by decantation with cold water, and then in the crucible, and is dried in the water-oven for five hours.

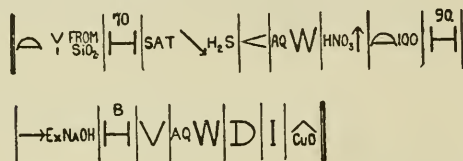


Analysis of Nickel.

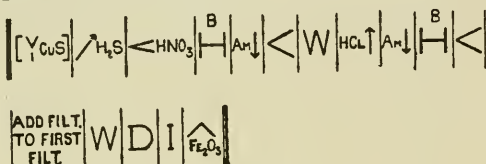
Silicon.—Dissolve 10 grms. in aqua regia, evaporate to dryness. Re-dissolve in hydrochloric acid, and again take to dryness. Take up with hydrochloric acid, dilute, filter, wash, dry, ignite, and weigh silica, SiO₂.



Copper.—Dilute filtrate from silica, heat 70°C ., and saturate with sulphuretted hydrogen gas. Filter off copper sulphide, wash, dissolve in small quantity of dilute nitric acid. Dilute resulting solution to 100 cc., heat to near boiling, add sodium hydrate solution in slight excess, and boil. Filter off precipitate, wash well with hot water, dry, ignite, and weigh as copper oxide (CuO).

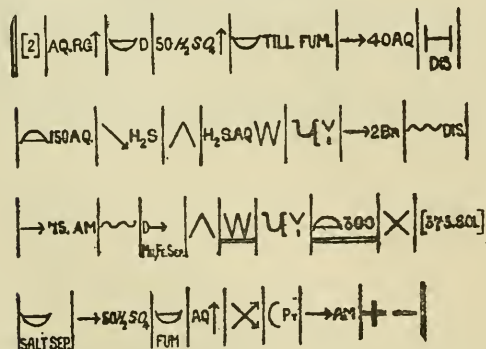


Iron.—Boil filtrate from copper sulphide until all sulphuretted hydrogen is expelled, add nitric acid to oxidise iron, and boil. Add ammonia in excess, heat to boiling, filter off ferric hydrate, and wash. Dissolve precipitate in hydrochloric acid, re-precipitate with ammonia, boil, filter (adding filtrate to first wash), dry, ignite, and weigh as ferric oxide, Fe_2O_3 .



Nickel.—Dissolve 2 grms. of sample in 30 cc. aqua regia, evaporate to dryness, re-dissolve in 50 cc. dilute sulphuric acid, evaporate till fumes are evolved. Add 40 cc. of water, heat until dissolved, dilute to 150 cc. with nearly boiling water, and saturate with sulphuretted hydrogen. Filter off copper sulphide, wash with sulphuretted hydrogen water, cool the filtrate, add 2 cc. bromine, shake until dissolved. Add about 75 cc. ammonia, shake vigorously, and digest until the hydrates of iron and manganese have separated out. Filter off precipitate, wash well with hot water, cool filtrate, dilute exactly 300 cc., and mix. Carefully measure out 37.5 cc. of the solution into a porcelain dish, evaporate until salts begin to separate out, add 50 cc. dilute sulphuric acid, and evaporate till white fumes are evolved.

Re-dissolve in a small quantity of water, make strongly alkaline with ammonia, and electrolyse.



These examples were selected at random from various text-books, and show clearly in what manner the method is likely to be useful.

In a short description of this kind it is of course impossible to convey to anyone the applicability and usefulness of such a system. Only experience in its use will show how useful it may become.

The chief uses have already been indicated, but the

method can easily be expanded to include bacteriological, biological, microscopical, and other branches of analysis, as well as to synthetical, physical, and other branches of pure chemistry.

The question of printing has been considered, and many useful ideas have had to be abandoned in order to comply with certain conditions set by the printers. A number of new symbols would have to be cast, but I have been assured that the cost would not be great. It is proposed to make symbolical operations equal in height to three lines of type. Working at this size, descriptions now written could be stated symbolically with a decided saving of space.

The greatest objection appears to be that the use in other languages would be very limited or impossible, but if the method ever got as far as general use no doubt solutions could be found for these difficulties.

115, Newgate Street, London, E.C.

THE DETERMINATION OF CADMIUM IN ZINC.

By W. COOPER.

COMMERCIAL samples of zinc are usually tested for the presence of iron, lead, copper, tin, arsenic, and cadmium.

The following method for the determination of cadmium has been found, after an extended trial, to give satisfactory results.

Five grms. of the sample are placed in a 200 cc. beaker, 150 cc. water and 7 cc. conc. sulphuric acid are added, and the metal is allowed to dissolve in the cold.

When treated in this manner nearly all commercial samples of zinc will dissolve over night, but occasionally it is found that some specimens are only acted upon very slowly by the acid; in these cases the action may be accelerated by placing a piece of platinum foil in contact with the zinc. When the evolution of hydrogen has ceased, the solution is carefully decanted into a 300 cc. conical flask and the black residue containing copper and lead is washed by decantation three times, 20 cc. of cold water being used for each wash and being added to the solution in the flask.

20 cc. of 1:3 sulphuric acid are added, the solution is diluted to 250 cc., and sulphuretted hydrogen is passed through for twenty minutes. The solution is allowed to stand in the cold for an hour or two, then filtered and the flask rinsed out three times, and the precipitate of cadmium and zinc sulphides washed three times with cold water. The precipitate is dissolved in a mixture of 5 cc. conc. HCl and 15 cc. bromine water, which is warmed in the flask and poured over the filter-paper; 5 cc. of 1:3 sulphuric acid are added and the solution is evaporated to fuming, diluted to 50 cc., cooled, and filtered from traces of lead sulphate after standing for an hour in the cold, the filter being washed three times with cold water; 20 cc. of 1:3 sulphuric acid are added, the solution is diluted to 200 cc., and sulphuretted hydrogen is passed for twenty minutes. The precipitate is filtered off, washed, and re-dissolved as before, and the solution is again evaporated to fuming with 5 cc. 1:3 sulphuric acid. 20 cc. of 1:3 sulphuric acid are added, the solution is made up to 200 cc. and sulphuretted hydrogen again passed for twenty minutes. The precipitate is filtered on to a filter-paper which has been washed with 200 cc. water containing 25 cc. 1:3 sulphuric acid, then washed free from acid, dried at 212°F . and weighed. The precipitate and paper, after drying at 212°F ., are weighed together, and the weight of precipitate obtained by difference. The weight of $\text{CdS} \times 0.778 \times 100 \div 5 = \text{Cd per cent.}$

To test the method two portions of 0.0146 gm. and 0.0050 gm. cadmium were weighed out, 5 grms. of pure zinc were added to each, and the metals were dissolved and treated as above.

The results given below were obtained.

Cadmium added.	Cadmium found.
0.0146 grm. = 0.29 per cent.	0.0140 grm. = 0.28 per cent.
0.0050 " = 0.10 " "	0.0050 " = 0.10 " "

The following are some results which have been obtained on commercial samples of zinc :—

Sample number.	Cadmium found (per cent.)	
I.	0.30	0.33
2.	0.20	0.17
3.	0.04	0.07
4.	0.22	0.22
5.	0.26	0.24
6.	0.13	0.14
7.	0.44	0.47
8.	0.09	0.10
9.	0.12	0.12
10.	0.24	0.25
11.	0.21	0.21

The black residue, insoluble in dilute sulphuric acid, and containing lead and copper, has repeatedly been dissolved in dilute nitric acid, evaporated to fuming with sulphuric acid, filtered from lead sulphate, and tested for cadmium. In no case has cadmium been detected.

POTASH SALTS.

SUMMARY FOR 1913.*

Compiled by W. C. PHALEN, United States Geological Survey, Washington, D.C.

(Continued from p. 244).

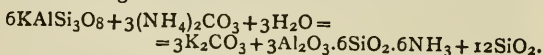
Potash Salts from the Silicate Rocks.

If the interest in the problem of the derivation of potash salts from the silicate rocks is to be judged from the number of processes which have been devised and patented, then the year 1913 showed no abatement in this interest. Several patents have been secured covering such processes, and a few articles on the subject have also appeared in the scientific literature. The more important of these processes are briefly reviewed below.

Process of Morse and Sargent.—H. W. Morse and G. W. Sargent (patent No. 1,041,327, dated October 15, 1912) have invented a process in which felspar is subjected at an elevated temperature, first, to the action of sulphate of lime (gypsum), and, second, to that of an alkaline chloride such as common salt or to a chloride of an alkaline earth metal as calcium chloride. There are produced oxides of sulphur, a soluble compound of potassium, and residual material which may be converted into Portland cement. According to the claims of the patentees, it is the production of the oxides of sulphur and the cement material in connection with that of the soluble potassium compound that makes possible the economical manufacture of the latter.

Process of Gelléri.—In the process of S. Gelléri (Patent No. 1,058,686, dated April 8, 1913) silicates are burned with lime or with an oxide or carbonate of an alkaline earth metal or magnesium for the purpose of decomposing the silicate and obtaining potash and cement clinker. After the silicates have been decomposed in this manner a large portion of the alkalis in them is still not in a condition whereby it may be leached with water. According to Gelléri's process this disadvantage is overcome by subjecting the silicates in a closed chamber to the action of ammonium carbonate vapour under pressure either after they have been burned with the oxides or carbonates of the alkaline earth metals or without this preliminary burning. By so doing the silicates are completely decomposed, and the whole of the alkali metal may be obtained in the form of an alkali carbonate by leaching

with water. The decomposition takes place according to the following reaction—



This process has the advantage that the whole of the ammonia in the ammonium carbonate is liberated, and, after the reaction is completed, the free ammonia may be used over again to make ammonium carbonate. This is most economically accomplished by saturating the ammonia with carbon dioxide from the furnace in which the silicates are burned with limestone. In order that a separate furnace may not be necessary to heat the silicates with ammonium carbonate, the furnace gases coming from the burning kiln may be used.

If the silicates have been burned with lime before being treated with ammonium carbonate, they contain all the constituents corresponding with the composition of Portland cement, so that it is possible to burn the silicates which have been decomposed and freed from alkalis to Portland cement by heating them again.

Process of Hart.—According to E. Hart (Patent No. 1,062,278, dated May 20, 1913), when felspar or similar rock is mixed with potassium or sodium sulphate and carbon and heated to fusion in a furnace, there is formed a soluble glass consisting of a potassium or sodium aluminium silicate. This glass may readily be decomposed by the addition of a suitable acid like sulphuric, which forms practically pure silica and a solution from which potassium and aluminium may be obtained in the form of common potash alum, leaving a mother-liquor which contains sulphates of potassium, sodium, or aluminium, some free sulphuric acid, and other sulphates formed by the action of the acid.

The mother-liquor is evaporated to dryness and fused with a suitable amount of carbon. The residue consists chiefly of aluminate of soda or potash, or both, or of one or more of these substances, together with alumina. If water be added to the residue, the aluminate of soda or potash will be largely dissolved, and there will be left an insoluble residue consisting chiefly of sulphide of iron, with possibly some alumina. From the solution of the aluminate of soda or potash alumina may be obtained by the usual methods.

Process of Bassett.—An invention by H. P. Bassett (patent No. 1,072,686, dated September 9, 1913), relates to the treatment of felspar or felspathic rock to obtain potash, and has particular reference to a process of not only obtaining potash salts from felspar or felspathic rock, but also of obtaining, in the form of a by-product, material which is adapted for use in manufacturing pottery.

Bassett has found that potash may be economically and satisfactorily obtained from felspar by treatment with salt alone, and that the potash salts and by-products of the reaction may be obtained in relatively pure form. In practice he adds to disintegrated and preferably finely ground felspar or felspar-bearing rock, about one-half its weight of sodium chloride. The mixture is next heated to a yellow heat, preferably from 800° to 900° C., in the presence of air, for about one to two hours. The mass is then dumped while still hot into a vat of water in the proportion of about two to five parts by weight of water to one part of the fused mass. The mass is then leached with water, and the potash and sodium salts are obtained in any desired manner, preferably by evaporation of the solution to dryness. The potassium and sodium salts are later separated, for example, by crystallisation. The leached residue, which corresponds in composition closely with that of the felspathic rock, except that the potassium is replaced by sodium, and that any iron present in the original rock will have been volatilised as iron chloride, and thus removed, is then dried and ground, the resulting product being a white mass that may be used for pottery or other purposes, such as a paper-filler or enamel ware. The felspar or felspar-bearing rock may be ground to

* From *The Chemical Engineer*, xx., No. 3.

any desired fineness before treatment, but preferably not less than 40 mesh; finer grinding than 100 mesh is unnecessary. The leached residue is dried and ground and is then ready for use.

Process of Cowles.—Early in 1913, A. H. Cowles (*Journ. Ind. and Eng. Chem.*, April, 1913, p. 331) described the results of certain experiments having to do with the extraction of potash alum and other soluble potash salts from the insoluble potash silicates. Cowles' experiments differ from those which have been described in that he mixes rock phosphate with the felspar, thus incorporating a second fertiliser element into the resulting mixtures.

In the first experiments potash felspar was ground with rock phosphate in such proportion as to furnish two molecular weights of lime to each molecular weight of silica in the felspar. The mixture was heated to a sintering temperature of about 1000° C., and the resulting product was leached with sulphuric acid. The resulting yield was practically 100 per cent. The products formed were insoluble dicalcium silicate, soluble potash alum, and orthophosphoric acid.

In the subsequent experiments less acid was used, and the results of the leaching gave a product containing all the potash and alumina in the felspar, but only part of the phosphoric acid. Duplicate experiments have been carried out in which hydrochloric instead of sulphuric acid was used. The solutions in the two cases gave either potash alum or the double chloride of potash and aluminium together with the phosphoric acid in the rock phosphate used in the experiment. Any iron present in the raw material used goes into solution with the aluminium and potash. From either the potash alum or the double chloride of aluminium and potash the opportunities for securing alumina are good. If the potash alum is heated to a dull red heat, the aluminium sulphate breaks down into alumina (Al_2O_3) and sulphuric acid (SO_3) and the potash sulphate may be leached away. If the double chloride of aluminium and potash is treated with water at a low temperature, hydrochloric acid is given off with the formation of alumina. The potassium chloride remains and may be leached away.

Private Enterprise in connection with the Extraction of Potash Salts from the Silicates.

The Spar Chemical Co., with headquarters at Baltimore, Md., has done some experimental work on the extraction of potash salts from the silicate rocks at a plant located at Curtis Bay, on the outskirts of the city. It is understood that the products are made according to the Thompson method, which is briefly outlined as follows:—

Thompson's process is described in patent No. 995,105, dated June 13, 1911. It consists first of grinding felspar rock so that it will pass through a 100-mesh sieve. The powdered rock is then mixed with an acid alkali sulphate and an alkali chloride, preferably acid sodium sulphate and sodium chloride, respectively. The proportions of the materials used are—Felspar rock, 5 parts by weight; acid sodium sulphate, 5 parts by weight; sodium chloride, 1·8 parts by weight. This mixture is heated from one to two hours at a bright red heat, and becomes thereby partly fused. The mass is then allowed to cool, is ground again, and is leached with water, which removes a mixture of sulphates of potassium and sodium. These salts are then separated by crystallisation. The reactions are believed to be as follows:—(a) The sodium acid sulphate reacts with the sodium chloride to produce hydrochloric acid gas and normal sodium sulphate; (b) the hydrochloric acid gas at the high temperature employed reacts on the felspar, producing potassium chloride; (c) the potassium chloride is in turn acted upon by more of the acid sodium sulphate, producing hydrochloric acid gas and potassium sulphate.

The yield of potash is ordinarily from 80 to 90 per cent of the potash in the rock. For the best results the temperature must be controlled within rather narrow limits.

(To be continued.)

AIR OZONATION.*

By MILTON W. FRANKLIN.

(Continued from p. 239).

II. Odour Destruction.

Casein.—In addition to the odour destruction tests outlined above and already published, further tests have since been made with casein and with tobacco smoke. The casein tests were undertaken with the object of destroying the odours arising from a factory producing about 500,020 lbs. casein per month. This material had a very bad, nauseating odour. In drying the material, air is passed over it or through it, and this takes up part of the disagreeable odour. This air then passes up a stack and out into the atmosphere, where it proves a nuisance to the neighbourhood. The problem is to destroy the odour before it passes up the stack.

Tests were made on the effluvium from the casein to determine whether ozone would affect it. For this purpose about 15 grms. were put into a Petri dish under a bell-jar. When the air had become saturated it was caused to displace the water in a Wolff bottle. A measured amount of this effluvium was then allowed to mix with a measured amount of ozonised air of known concentration. Several tests were made, using various quantities of ozone, any odour due to excessive ozone being removed with ferrous sulphate. In each case the odour due to casein was destroyed. The least quantity of ozone which sufficed was 1·84 mg. per litre of effluvium; 1·75 mg. per litre left a slight trace of the odour. The results are presented herewith.

1. 1 l. of effluvium was entirely deodorised by 0·47 mg. of ozone, with a distinct excess of ozone.

2. 11 l. of effluvium were entirely deodorised with 0·41 mg. of ozone or 0·037 mg. per l. with excess of ozone.

3. 14 l. of effluvium were deodorised with 0·171 mg. of ozone or 0·012 mg. per l. with excess of ozone.

4. 0·0057 mg. ozone per litre of effluvium materially lessened the odour but did not destroy it entirely.

The proportion of air to casein in the experiment was less than in the most unfavourable case that the factory conditions exhibit. The casein used was in a much more advanced state of decay and probably had odours that were far stronger than are ever obtained at the factory. Complete elimination of the odour was the object in the experiment, and this was obtained at will. The qualitative tests which preceded the quantitative tests demonstrated that actual destruction and not masking of the odour was attained.

Smoke.—The destruction of the odour of stale tobacco smoke and of old moist cigar stumps has always constituted a most graphic illustration of the power of ozone. Rooms in which much smoking has occurred retain the odour of tobacco in the walls, hangings, and furnishings, and this odour is enduring and persistent. Experiments in which it was shown that the odour imparted to cheese cloth by tobacco smoke could be destroyed by ozone have been published in the previously cited paper (*Heating and Ventilating Magazine*, N.Y., x., Nos. 10 and 11). There seems to be some difference of opinion, however, regarding the effect of ozone on the smoke present in an occupied room during the actual smoking, and where the ozone is of such strength as to be comfortably borne by the room occupants.

Hill and Flack (*Proc. Roy. Soc.*, B, lxxxiv., p. 404) noted that the apparent density of the smoke diminished and that the odour disappeared. Kisskalt, Schwartz, and Münchmeyer (*Chemiker Zeit.*, 1912, No. 129) noted a lessening in the smoke density and total disappearance of the odour. Cramer (*Gesundh. Ing.*, 1909, p. 498) states with regard to experiments performed on a large scale—

* From *Journal of Industrial and Engineering Chemistry*, vi., No. 10.

"All that could be clearly demonstrated was the fact that the smoke haze became appreciably lighter and that the pungent characteristic of the smoke disappeared, rendering it no longer irritating to the eyes."

Czaplewski (*loc. cit.*) states—

"In our own tests with stronger ozone concentrations, cigarette smoke was entirely destroyed in a room so as not to be perceived by a person entering the room from the outside. There was no 'after' smell and tobacco smoke on clothing is disposed of by ozone."

Smoke consists of particles of carbon and of various volatilised pungent and aromatic substances. Only the latter give taste, smell, and irritating properties to smoke, the carbon contributing most of the visibility. The volatile elements in smoke exist in the gaseous form, *i.e.*, in a state of molecular subdivision, but the carbon particles exist in the shape of molecular aggregates, each of infinite size compared with the molecules themselves, otherwise they would not be visible. Ozone can combine only with the volatile elements in smoke. It thus renders it odourless, tasteless, and incapable of causing irritation, but it cannot burn the carbon which in any event is totally inert and harmless. Numerous tests with actual smoke have shown this to be true.

In my own tests I have observed that when the ozone is turned on in a smoke-laden atmosphere the density of the smoke lessens and the odour and pungency disappear, the smoke being entirely undetectable excepting for its visibility. For some time I have suspected that the apparent diminution in visual density might be due to stirring up of the air by the fan which is attached to all the ozonators with which I have experimented in this direction. Some experiments were performed to determine whether or not ozone actually diminished the smoke density. Wolff bottles of 2 l. capacity, and furnished with a tubulure at the base, were filled with water. One of the necks was stoppered and the other attached by a rubber tube to a glass funnel inverted over a quantity of burning tobacco. The tobacco was burned on a thin, flat iron plate by means of a gas burner placed underneath. The funnel was supported with its rim about $\frac{1}{2}$ inch above the plate and directly above the tobacco. When the tubulure was opened and water permitted to flow from the Wolff bottle, the air which replaced the water flowed under the edge of the inverted funnel and over the burning tobacco, whose smoke was carried along with the air. In this manner each of two bottles was half filled with a dense cloud of smoke. One of these bottles was then connected to the ozone line and the remaining water replaced by ozonised air, leaving about $\frac{1}{2}$ inch of water in the bottom of the bottle. Into the other bottle atmospheric air was introduced in the same manner. The bottles were then shaken to cause the water to mix the smoke and air thoroughly, and the bottles were placed side by side on a shelf and observed after various periods of time. The results are presented in the following tabulation:—

I. Test No.	II. Ozone mgm.	III, 15 min.	IV, 30 min.	V, 1 hr.	VI, 4 hrs.
1.	1.05	Slightly clearer.	Slightly clearer.	Marked clearing (slight).	Marked clearing.
2.	0.92	Slightly clearer.	Slightly clearer.	Slightly clearer.	Marked clearing.
3.	1.10	No differ- ence.	Slightly clearer.	Slightly clearer.	Slightly clearer.
4.	1.13	Slightly clearer(?)	Slightly clearer.	Marked clearing.	Marked clearing.
5.	0.96	Slightly clearer.	Slightly clearer.	Slightly clearer.	Marked clearing (slight).

The remarks under columns III., IV., V., and VI. refer to the bottles containing smoke, air, and ozone, respectively compared with the corresponding bottles containing only

air and smoke. The tobacco was of a standard inexpensive "cut plug" variety sold in ten cent packages, and was rather sweet, strong, and moist. The amount of tobacco was completely burned, the entire gaseous products of combustion entering the Wolff bottle. There was considerable condensation on the funnel at first, but later this decreased greatly, as ascertained on weighing the funnel, and the results given are of the later tests. The smoke in the bottles was much denser than could be obtained in any room by persons smoking.

It will be seen that in the bottle containing ozone the smoke, in general, cleared sooner than that in the bottle containing only air. The difference, though always unmistakable after several hours, was only occasionally quite marked. The amount of clearing after the lesser periods of time was so slight as often to be questionable, but in general it can be said that the ozone makes a slight reduction in the smoke density. In each case the smoke settled slowly in a cloud, leaving the top of the bottle clear. The "conglomeration" noted by Cramer (*Gesundh. Ing.*, 1909, p. 498) was seen only in one test (No. 3) and then only faintly.

It might be concluded from the above tests that ozone is capable of lessening somewhat the visual density of tobacco smoke, but when it is remembered that the ozone concentration was about 1 grm. per cbm. it hardly seems probable on first thought that the clearing noted when ozone at a concentration not exceeding 1 mgm. per cbm. is turned into a smoky room, is due alone to the action of the ozone. However, a consideration of the quantities involved indicates that this may well be true. In the tests the products of combustion of 2 grms. of tobacco were collected in the space of 2 l. in approximately two minutes. This would be equivalent to burning 41 kg. tobacco in a room of 41 cbm. (12 ft. $\times$ 12 ft. $\times$ 10 ft.) in two minutes. Five men smoking pipes in such a room would burn only 4.3 grms. in the same period. Thus the ratio of tobacco consumption in the above described laboratory tests and in this hypothetical case is approximately 10,000:1, while the ratio of the ozone concentrations is only 1000:1, or in a similar actual case occurring in practice the amount of ozone would be about ten times more in proportion to the tobacco than in the tests described. Besides this there would be approximately 10,000 times as much air for the smoke to diffuse into, and a marked clearing action is exercised by the air, which may be intensified by the action of the ozone. The estimates of the amounts of tobacco consumed are based on measurements of ten pipes and on timing different smokers. The average amount of tobacco (of the kind used in the experiments) held by the pipes was 1.62 grms. and the average time of smoking was thirty eight minutes. In all cases the odour of the smoke was markedly or even completely removed, leaving it odourless, tasteless, and with no power to irritate the mucous membrane of the eyes, nose, or mouth.

Fragments of cloth were cut into strips 5 cm. $\times$ 8 cm. and suspended in a bell-jar having a tubulure at the bottom and a neck at the top. The latter was connected on an aspirator and tobacco smoke was drawn in at the tubulure. After the smoke from 2.5 grms. of tobacco had permeated the cloth strips the latter were removed and examined; they smelled strongly of tobacco. They were then replaced in the bell-jar and ozonised air was drawn through for varying periods of time. The concentration was 1.03 mg. per cbm. The results were as follows:—

Test No.	Material.	Result.	Time. Min.
1.	Cheese-cloth (thoroughly washed)	Thoroughly deodorised.	9
2.	Cheviot (cut from an old suit) ..		29
3.	Satin (cut from lining of old suit)		18
4.	Duck (new)		6

No. 1 became most strongly odorous with the same exposure as the others. After a rest of twelve hours No. 2 experienced a slight, though distinct, return of odour,

which, however, disappeared finally within five minutes' additional ozonisation. The comparative thickness and microscopic perplexity of the cloth undoubtedly accounts for this phenomenon.

(To be continued.)

SHEFFIELD UNIVERSITY SCIENTIFIC ADVISORY COMMITTEE.

IN consequence of the situation brought about by the War, and of the opportunity afforded for an extension of our export trade, the Council of the University have approved the formation of a University Scientific Advisory Committee, consisting of the members of the Science and Applied Science Faculties and of the Department of Economics, in the hope that such a Committee will be able to render service to local manufacturers in dealing with the new conditions presented to them, and they suggest that, as far as possible, the resources of the University shall be available for such a purpose in one or other of the following ways:—

1. By directing manufacturers, experimenters, and inventors to scientific and technical literature bearing upon the difficulties with which they are presented in dealing with new problems.
2. By putting manufacturers into communication with suitable scientific and practical expert opinion, and giving such other help or advice as it may be within the power of the staff to give, on the understanding that no work should be done by the Committee which could readily, and in the ordinary way of business, be dealt with by local professional experts.

Any person residing within the Sheffield University area desiring the assistance of the Committee should apply in the first instance by letter to Dr. W. E. S. TURNER, Secretary of the Sheffield University Scientific Advisory Committee, Applied Science Department of the University, St. George's Square.

EFFECT OF THE WAR ON THE COLOUR-USING INDUSTRIES.

THE Council of the Society of Dyers and Colourists appointed some two months ago a committee to consider ways and means of dealing with the shortage of chemicals and dye-stuffs caused by the war. The Committee has held frequent meetings, at which the possibility of meeting the emergency and of obtaining future supplies has been discussed.

Lord Moulton, a member of the Board of Trade Committee on Chemical Products, and Chairman of the Special Committee appointed by that Board to deal with the question of the supply of chemicals and colours, has had interviews with several members of the local committee, and this committee has now obtained direct representation on the Board of Trade Committee in the person of Dr. Alfred Rée.

Statistics are being collected from the principal colour users with a view to ascertaining the approximate consumption of the chief individual dye-stuffs, of which the bulk was formerly obtained from Germany. When this information has been obtained it will be possible to form a much clearer idea of the variety and approximate quantities of intermediate products necessary for making the dye-stuffs annually required.

The Committee is of opinion that every assistance should be given to English makers to enable them to extend their manufacturing operations.

The work of the local committee is of considerable magnitude, but it is hoped that some definite issues will soon materialise.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 5, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"On Acquired Radio-Activity." By Sir WILLIAM CROOKES, O.M., P.R.S.

Various objects—diamond, ruby, garnet, quartz, gold, platinum, &c., also the phosphorescent substances yttria, calcium sulphide, zinc blende, and barium platinocyanide—are bombarded in a high vacuum by cathode rays, and in no case can any permanent activity be recognised either by photographic or electrical means.

Exposure to radium emanation confers temporary radio-activity on all bodies that have been tried, apparently due to the condensation of the emanation on the surface. This transient activity can be completely removed by washing in dilute acids.

Many substances become coloured by direct exposure to radium, the colour depending on the substance. Diamond takes a full sage-green tint, the depth of tint depending on the time of exposure to the radium.

In addition to change of colour, diamond also becomes persistently radio-active, continuously giving off α -, β -, and γ -rays. The acquired colour and activity withstand the action of powerful chemical agents, and continue for years with apparently undiminished activity.

Removing the surface by mechanical means removes both colour and radio-activity.

The appearance of an auto-radiograph, made by placing an active diamond crystal on a sensitive photographic plate, and the visual examination of its "scintillation" luminosity, suggest that there is a special discharge of energy from the corners and points of the crystal.

"Luminous Vapours Distilled from the Arc, with Applications to the Study of Spectrum Series and their Origin." (II.). By Hon. R. J. STRUTT, F.R.S.

(1) The conducting properties of a luminous jet of mercury vapour distilled from the arc *in vacuo* have been examined. The current depends on the shape and position of the cathode introduced into the jet, and is independent of the position of the anode. In the case where the anode is reached first by the stream of vapour, and a net electrode is used as cathode, all the positive ions may be taken out of the vapour that passes through the cathode. There is saturation of the current in the layer near the cathode. On the other hand, recombination proceeds in the rest of the space between cathode and anode, for the electric force is concentrated near the cathode, and near the anode is not strong enough to take out all the negative ions.

(2) The luminosity of the jet is unaffected by the removal of negative ions at the anode, but is quenched by removal of positive ions at the cathode. Although the removal of negative ions in the latter case is not complete, it is considerable enough to show conclusively that the luminosity is independent of the number of negative ions present. Thus the luminosity is not due to recombination of ions. It seems necessary to assume that the luminous centres in the jet are survivors of those generated in the arc itself, in spite of the appreciable time (1/1000 second) necessary for the vapour to travel down the tube. We must suppose these centres to be positively charged to account for their removal at the cathode.

(3) Experimenting with other metals as well as mercury, it is found that the various lines of a spectrum are not in all cases equally extinguished when the jet of luminous vapour passes through a negatively electrified net. Thus the lines of the subordinate series of the sodium spectrum apparently all lose intensity in the same ratio; but the D line of the principal series is much less affected. Thus

it is inferred that the luminous centres emitting the principal series are not the same as the luminous centres emitting the subordinate series. Analogous differences have been observed in the line spectra of magnesium and zinc.

(4) The jets formed by arsenic and antimony, which show band spectra consisting of large numbers of uniformly spaced bands, are not quenched by passing through a negatively electrified net. The luminous centres appear, therefore, to be unchanged in these cases.

"Production of Neon and Helium by the Electrical Discharge." By Prof. J. N. COLLIE, F.R.S., H. S. PATTERSON, and I. MASSON.

"Flow of Viscous Fluids through Smooth Circular Pipes." By Prof. C. H. LEES, F.R.S.

"Quantitative Measurements of the Absorption of Light. I.—The Molecular Extinctions of the Saturated Aliphatic Ketones." By F. O. RICE.

The absorptive power of fourteen of the saturated aliphatic ketones has been measured quantitatively with an ultra-violet spectro-photometer. It was found that previous observations by other authors were inaccurate owing to the presence of impurities in the ketones. The general results of the present observations are considered from two points of view, namely, the position of the absorption band and the maximum absorptive power. The wave-length of the absorption band depends upon the number and position of the alkyl groups in the side-chain, and tends to increase with the number of CH_3 or CH_2 groups. In the case of the normal side-chains a limiting value for the wave-length of the absorption band is reached, and may be expressed as follows: The ketones of the general formula $\text{CH}_3\text{—CO—CH}_2\text{—CH}_2\text{—R}$, where R is any alkyl radical, exhibit an absorption band with centre at $\lambda = 2790$ Angströms. Further, the absorption bands of all the ketones are geometrically similar. Again, all the ketones examined, with the exception of acetone and methyl ethyl ketone, exhibit the same absorptive power expressed by a molecular extinction co-efficient of 21.2 . The deviation of acetone and methyl ethyl ketone may be explained by their being associated. Assuming that the absorptive power of the complex molecule varies inversely as the number of simple molecules it contains, the association factors of acetone and methyl ethyl ketone are found to be 1.24 and 1.09 respectively. Ramsay and Shields by their method found the value of 1.26 for acetone, which is in close agreement. The results do not conform to the theory put forward by Henderson and Heilbron, which involves a labile hydrogen atom. Hexamethylacetone, with no labile hydrogen when purified, exhibits an absorption band similar to all the other ketones, a fact which was not observed by these authors. A satisfactory explanation is to be found in the existence of an electromagnetic field surrounding the CO group, a field which is modified by the neighbouring alkyl groups.

"Ignition of Gases by Condenser Discharge Sparks." By Prof. W. M. THORNTON.

"Spark Spectrum of Nickel under Moderate Pressures." By E. G. BILHAM.

CHEMICAL SOCIETY.

THE Council has ordered the following letter and report to be printed in the *Journal and Proceedings* of the Society:—

Whinfield, Salcombe, S. Devon,
Sept. 18th 1914.

GENTLEMEN,—I have the honour to forward the Annual Report of the International Committee on Atomic Weights for 1915, which is submitted for publication in the Society's *Transactions and Proceedings*, as hitherto. Some delay has occurred in presenting it owing to the disturbance of the postal arrangements on the Continent in

consequence of the war, and to the illness of Prof. Urbain.

The Report deals with all the determinations of atomic weights which have been published since the issue of the preceding Report; but, in accordance with the resolution of the Eighth International Congress of Applied Chemistry, no change in the official table of atomic weights will be made until after the meeting of the next Congress. It is recommended, therefore, that the table accompanying the Report for 1913 should be reprinted without alteration.

I have appended the signatures of Professors Ostwald and Urbain as desired by them, subject to a qualification by the latter which he proposes to introduce in the French translation of the Report in connection with the atomic weights of ytterbium and lutecium.—I am, Gentlemen, your obedient Servant,

T. E. THORPE.

The Hon. Secretaries, the Chemical Society, London.

Annual Report of the International Committee on Atomic Weights, 1915.

The Council of the International Association of Chemical Societies, with which the Committee on Atomic Weights is now affiliated, recommended, at its meeting in September, 1913, that the Annual Report of said committee should be published in August. The present report, therefore, is submitted in compliance with that recommendation, although delays due to the difficulties of correspondence may sometimes prevent simultaneous publication in all countries.

Since the report for 1914 was prepared, a number of new atomic weight determinations have been published. These may be briefly summarised as follows:—

Silver, Sulphur, and Chlorine.—Scheuer (*Arch. Sci. Phys. Nat.*, 1913, [iv.], xxxvi., 381) dissolved pure silver in sulphuric acid, and collected and weighed the sulphur dioxide given off. The weighed sulphate was then converted into chloride by heating in a current of gaseous hydrochloric acid. Three ratios were thus determined, which gave the three desired atomic weights, independent of all former determinations. The results obtained are $\text{Ag} = 107.884$, $\text{S} = 32.067$, $\text{Cl} = 35.460$. The value for silver is rather high; the other values agree with those generally accepted.

Calcium.—Echsner de Coninck (*Bull. Acad. Roy. Belg.*, 1913, 222) has determined the atomic weight of calcium by conversion of the carbonate into the sulphate. His final value is $\text{Ca} = 40.13$.

Barium.—Also re-determined by Echsner de Coninck (*Rev. Gén. Chim. Pure Appl.*, 1913, xvi., 245). Barium carbonate was dissolved in nitric acid, and the carbon dioxide so evolved was weighed. The value found was $\text{Ba} = 137.36$.

Copper.—Atomic weight determined by Echsner de Coninck and Ducelliez (*Rev. Gén. Chim. Pure Appl.*, 1913, xvi., 122). Copper was oxidised by nitric acid, and the oxide was weighed. In five experiments they found $\text{Cu} = 63.523$ to 63.605 ; in mean, 63.549 . These atomic weight determinations by Echsner de Coninck are published in the briefest possible way, without any of the details that are commonly regarded as essential. How were the substances purified? Were the weights reduced to a vacuum?

Cadmium.—Quinn and Hulett (*Journ. Phys. Chem.*, 1913, xvii., 780) have re-determined the atomic weight of cadmium by electrolysis of the chloride and bromide. In each series the cadmium was collected and weighed in mercury. From the chloride, with $\text{Cl} = 35.458$, $\text{Cd} = 112.32$. From the bromide, with $\text{Br} = 79.92$, $\text{Cd} = 112.26$. These values agree well with those previously found by Perdue and Hulett, and by Laird and Hulett, but are much lower than the value (Baxter's) adopted in the table. The cause of the difference is yet to be satisfactorily explained, but it must be due to a constant error in one or the other of the methods employed. A change in the table would be premature.

International Atomic Weights. (1913).

		O = 16.
Aluminium	Al	27.1
Antimony	Sb	120.2
Argon	A	39.88
Arsenic	As	74.96
Barium	Ba	137.37
Bismuth	Bi	208.0
Boron	B	11.0
Bromine	Br	79.92
Cadmium	Cd	112.40
Cæsium	Cs	132.81
Calcium	Ca	40.07
Carbon	C	12.00
Cerium	Ce	140.25
Chlorine	Cl	35.46
Chromium	Cr	52.0
Cobalt	Co	58.97
Columbium	Cb	93.5
Copper	Cu	63.57
Dysprosium	Dy	162.5
Erbium	Er	167.7
Europium	Eu	152.0
Fluorine	F	19.0
Gadolinium	Gd	157.3
Gallium	Ga	69.9
Germanium	Ge	72.5
Glucinum	Gl	9.1
Gold	Au	197.2
Helium	He	3.99
Holmium	Ho	163.5
Hydrogen	H	1.008
Indium	In	114.8
Iodine	I	126.92
Iridium	Ir	193.1
Iron	Fe	55.84
Krypton	Kr	82.92
Lanthanum	La	139.0
Lead	Pb	207.10
Lithium	Li	6.94
Lutecium	Lu	174.0
Magnesium	Mg	24.32
Manganese	Mn	54.93
Mercury	Hg	200.6
Molybdenum	Mo	96.0
Neodymium	Nd	144.3
Neon	Ne	20.2
Nickel	Ni	58.68
Niton (radium emanation)	Nt	222.4
Nitrogen	N	14.01
Osmium	Os	190.9
Oxygen	O	16.00
Palladium	Pd	106.7
Phosphorus	P	31.04
Platinum	Pt	195.2
Potassium	K	39.10
Praseodymium	Pr	140.6
Radium	Ra	226.4
Rhodium	Rh	102.9
Rubidium	Rb	85.45
Ruthenium	Ru	101.7
Samarium	Sa	150.4
Scandium	Sc	44.1
Selenium	Se	79.2
Silicon	Si	28.3
Silver	Ag	107.88
Sodium	Na	23.00
Strontium	Sr	87.63
Sulphur	S	32.07
Tantalum	Ta	181.5
Tellurium	Te	127.5
Terbium	Tb	159.2
Thallium	Tl	204.0
Thorium	Th	232.4
Thulium	Tm	168.5
Tin	Sn	119.0

O = 16.

Titanium	Ti	48.1
Tungsten	W	184.0
Uranium	U	238.5
Vanadium	V	51.0
Xenon	Xe	130.2
Ytterbium (Neoytterbium)	Yb	172.0
Yttrium	Yt	89.0
Zinc	Zn	65.37
Zirconium	Zr	90.6

Mercury.—Taylor and Hulett (*Journ. Phys. Chem.*, 1913, xvii., 755) prepared mercuric oxide by heating pure mercury in oxygen. Weighed amounts of the oxide were then decomposed by heating it with metallic iron, and the mercury was collected and weighed. From the data thus obtained, $Hg = 200.37$. This, as in the case of cadmium, is lower than the recognised value, and its acceptance or rejection must await further evidence.

Vanadium.—Atomic weight re-determined by Briscoe and Little (*Proc.*, 1914, xxx., 64; *Trans.*, 1914, cv., 1310) from analyses of the oxychloride, $VOCl_3$. The mean value found was $V = 50.950$, but 50.96 is preferred.

Selenium.—Jannek and Meyer (*Zeit. Anorg. Chem.*, 1913, lxxxiii., 51) determined the atomic weight of selenium by oxidising Se to SeO_2 . The mean of ten experiments gave $Se = 79.140$.

The same constant was deduced by Bruylants and Bytebier (*Bull. Acad. Roy. Belg.*, 1912, 856) from the density of selenium hydride, SeH_2 . In four series of experiments, the weight of a litre of the gas at 0° and 760 mm. was found to be 3.6715 grms. For the weight of a litre of oxygen under the same conditions they found 1.4295 grms. (According to Germann, *Comptes Rendus*, 1913, clvii., 926, the normal litre of oxygen weighs 1.42900 grms.). By the method of limiting densities, and with $H = 1.008$, $Se = 79.18$, which is near the value given in the table.

Tellurium.—Dennis and Anderson (*Journ. Am. Chem. Soc.*, 1914, xxxvi., 882) purified tellurium by preparing the hydride, TeH_2 , from aluminium telluride, and condensing the gas to solid at the temperature of liquid air. From the hydride the metal was obtained by heating to 500° . Thirty-one conversions of Te thus prepared into TeO_2 gave in mean $Te = 127.6$. Other determinations by a volumetric method gave a lower value, near 127.50. The authors conclude that the higher hypothetical "divtellurium" does not exist.

Scandium.—Lukens (*Journ. Am. Chem. Soc.*, 1913, xxxv., 1470) prepared scandium oxide from Colorado wolfram. By calcination of the sulphate to oxide he found $Sc = 44.59$ and 44.77 . The material was probably not quite pure.

Yttrium.—Meyer and Weinheiser (*Ber.*, 1913, xli., 2672), by conversion of yttrium oxide into sulphate, found $Yt = 88.75$. By the reverse process they found $Yt = 88.74$. Corrected to a vacuum, this becomes 88.70.

Ytterbium and Lutecium.—Atomic weights re-investigated by Auer von Welsbach (*Monatsh.*, 1913, xxxiv., 1713). For ytterbium (aldehydebarium) he found $Yb = 173.00$. For lutecium (cassiopeium), $Lu = 175.00$.

Iridium.—Holzmann (*Sitzungsber. Phys.-med. Soz. Erlangen*, xlv., 84) made four reductions of the salt $(NH_4)_2IrCl_6$ in hydrogen, and found $Ir = 193.42$. This is higher than the accepted value, and not conclusive enough to justify a change.

Helium.—Heuse (*Ber. Deut. Physikal. Ges.*, 1913, xv., 578), in seven determinations of the density of helium, finds the weight of a normal litre to be 0.17856 gm. Hence, by the method of limiting densities, $He = 4.002$.

Neon.—From two determinations of the density of neon, Leduc (*Comptes Rendus*, 1914, clviii., 864) finds $Ne = 20$.

No changes of serious importance seem to be needed in the atomic weight table. Possibly the values for yttrium, ytterbium, helium, and neon should be changed, but such action may well be deferred until next year. Some

experiments by Richards and Cox (*Journ. Am. Chem. Soc.*, 1914, xxxvii., 819) on the purity of lithium perchlorate also suggest a possible lowering in the atomic weight of silver, namely, from, 107.88 to 107.871.

(Signed) F. W. CLARKE.
W. OSTWALD.
T. E. THORPE.
G. URBAIN.

NOTE.—Since this report was finished and approved, Prof. Urbain has informed us that, jointly with M. Blumentfeld, he has re-determined the atomic weight of neoytterbium with great care. The earth was subjected to many fractionations, and each fraction was studied magnetically and spectroscopically. The value found for the atomic, the mean of thirteen determinations, was 173.50. He suspects that the "aldebaranium" studied by Auer von Welsbach contained an element of lower atomic weight, probably thulium. Urbain's paper will be published in the near future, perhaps before this report appears.

F. W. C.
T. E. T.

SOCIETY OF CHEMICAL INDUSTRY. (NOTTINGHAM SECTION).

THE first meeting of the Nottingham Section of the Society of Chemical Industry took place at University College, Nottingham, on Wednesday, October 28, when Mr. JOHN WHITE, F.I.C., County Analyst for Derbyshire, the Chairman of the Section, gave his Inaugural Address on "*The Work of the Public Analyst in Relation to Manufactured Products.*"

Mr. White adopted an uncompromising attitude on the question of the purity of food substances. He pointed out that the day of the crude "faker" and adulterator was past. The public analyst had now to deal with scientific food adjustment, which required special technical skill in its working and detection. He referred to the historic controversy which centred round the question of "milk blended butter," which in its original form contained about 25 per cent of water. Special legislation was enacted to deal with the question, and the name "milk blended butter" was now illegal.

The so-called polishing of rice and pearl barley was a wholly unnecessary practice, in which a thin coating of talc or french chalk is applied, oil being the adhesive used. Special apparatus is made in Germany for the purpose. The Local Government Board's limit of 0.5 per cent talc was adversely referred to.

Amongst other questions touched on was vinegar in relation to its preparation from mixed grains; the substitution of cotton-seed oil in the sardine industry was condemned. Specially interesting were his references to the margarine question, in which it was pointed out that cocoanut oil was more and more replacing the animal fats formerly employed. In this connection the fact that Siberian butters possessing a low content of volatile fatty acids at one time threatened to make it impossible to detect addition of margarine to butter was referred to.

Touching on the question of the bleaching of flour, Mr. White suggested that the present desire for whiteness was a demand created by the manufacturer in order to obtain enhanced prices for somewhat inferior products. In regard to improvers in flours his view was that the sole object of their use was to enable a larger number of loaves to be made from a given quantity of flour.

Baking powders owe their activity to the evolution of carbon dioxide, and yet some baking powders on the market were practically devoid of gas evolving properties. The paper was keenly discussed.

Mr. PENTECOST, in opening, congratulated Mr. White on his accession to the Chairmanship of the Section. The points round which the discussion centred were margarine,

the substitution of cotton-seed and other oils in the sardine industry, the materials used by millers, &c.

Mr. TIMMANS instanced an interesting point in connection with the conservatism of the consumer on account of the treatment that bones now undergo, degreasing and degelatinising—dissolved bones of modern times is not such a dark coloured product as formerly, and the point gave him considerable trouble as a sulphuric acid manufacturer.

Another speaker referred to the whiteness of food products, and suggested that the question at bottom was an æsthetic one, and that many people really preferred a truly white bread, a white tapioca in place of the yellowish sago, and so on.

Mr. ARCHBUTT mentioned that during the last year or two the olive oil crop had been under the average, and suggested that the replacement of olive oil by sardine packers had a certain necessity.

Mr. WHITE, in reply, dealt with the various points raised, and stated that in his view once the manufacturer had created a standard he had no freedom to change that standard.

NOTICES OF BOOKS.

Methods of Quantitative Organic Analysis. By P. C. R. KINGSCOTT, D.I.C., A.R.C.Sc., A.I.C., B.Sc. (Lond.), and R. S. G. KNIGHT, D.I.C., A.R.C.Sc., A.I.C., B.Sc. (Lond.). London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1914.

QUANTITATIVE organic analysis presents special difficulties to students owing to the fact that there are comparatively few generally applicable methods, such as are available in organic analysis, and this book, which deals adequately with the subject, will be found very useful. Methods of determining molecular weight are first described in sufficient detail for the purposes of the average student who has had a good training in inorganic analysis, and then a very full account is given of the ultimate analysis of organic compounds. Here all the most important modern methods are described, and great attention is paid to modifications of details. The identification of certain groups—carboxyl, methoxy, &c.—is then treated, and finally the analysis of some compounds of technical importance, such as sugars, dyes, indigo, oils, and fats is described. The work described is not arranged according to difficulty, and hence the student would probably not find it advisable to work straight through the book.

Chemical Engineering. By J. W. HINCHLEY, A.R.S.M., Wh.Sc. London: J. and A. Churchill. 1914.

THE sub-title of this book, "Notes on Grinding, Sifting, Separating, and Transporting Solids," indicates its scope, and the author has contrived to give in a very limited space a good deal of useful information relating to the various processes. The economical aspects are kept before the reader, and the subject is treated concisely and practically. The book, which is a reprint with some additions of a series of articles which appeared in the *Chemical World*, will serve as an introduction to the subject for the student of chemical engineering.

Van Nostrand's Chemical Annual, 1913. Edited by JOHN C. OLSEN, A.M., Ph.D. Third Issue. London: Constable and Co., Ltd. 1914.

IN the third issue of this handbook all the numerical and other data have been revised and corrected, and many new tables have been added. These include solubility of gases in water, fuming sulphuric acid and alcohol, and other specific gravity tables. The section on thermochemistry has been much enlarged, and tables of heats of formation and neutralisation have been added. A

section on stoichiometry has been inserted, and many problems, some worked and others unworked, are now given.

History of the Institute of Chemistry of Great Britain and Ireland, 1877-1914. Compiled by RICHARD B. PILCHER.

This history of the Institute of Chemistry contains a full account of the work it has done since its inception in 1877. The value of its labours in organising professional chemists and raising the standard of their efficiency can hardly be over-estimated, and the Institute has taken a very important part in the encouragement of systematic and thorough education in chemistry. Much of the correspondence concerning the foundation of the Institute which appeared originally in the *CHEMICAL NEWS* is reproduced, and the addresses of the President and accounts of the important transactions at the annual meetings are included.

Report on the Progress and Condition of the United States National Museum for the year ending June 30, 1913. Washington: Government Printing Office. 1914.

The Report of the United States National Museum shows that it is a well planned and admirably managed institution which has reached a high state of efficiency. From an educational point of view it is clearly of immense value to the inhabitants of Washington, and curators and governors of museums will be able to learn a good deal from the study of the details of its organisation.

CORRESPONDENCE.

DISPLACING GERMAN TRADE.

To the Editor of the Chemical News.

SIR,—On behalf of the Sheffield University Scientific Advisory Committee, I shall be glad to receive from manufacturers information concerning any new apparatus, plant, or material which may be put on the market with the view of transplanting or substituting that which has hitherto been supplied from German sources.

The Committee is constantly receiving enquiries concerning apparatus, machinery, and material, and for this reason will welcome information of the character above mentioned.—I am, &c.,

W. E. S. TURNER, Secretary to the Committee.

University of Sheffield,
Department of Applied Science,
St. George's Square, Sheffield.
Nov. 11, 1914.

MISCELLANEOUS.

"All about Ozonair."—This pamphlet describes shortly the apparatus which the Ozonair Company has designed for ozonising air and for the commercial production of ozone for all purposes. The principles involved are discussed in outline, and the use of ozone in deodorising, water purification, bleaching, conditioning, &c., is explained. The pamphlet and other similar publications dealing with the application of ozonair apparatus in various industries can be obtained from the offices of the Company, 96, Victoria Street, S.W.

Society of Chemical Industry (Liverpool Section).—The First Meeting of the Session will be held in the Chemistry Theatre of the University, on Wednesday, Nov. 25, at 8 p.m. A Discussion will be opened by the Chairman on "The Future Position and Prospects of the British Chemical Trade, and the Question of Concerted Action on the part of Manufacturers." As this matter is one of national importance, and particularly affects members of this Society, the Committee hope that members of the

Section will endeavour to be present at this meeting, and that they will be prepared to take part in the Discussion.

Royal Institution.—The Eighty-ninth Christmas Course of Juvenile Lectures, founded at the Royal Institution in 1826 by Michael Faraday, will be delivered this year by Prof. C. V. Boys, F.R.S., his title being "Science in the Home." The lectures will be experimentally illustrated, and the subjects are as follows:—"Mechanics in the Home," Tuesday, Dec. 29; "Chemistry in the Home," Thursday, Dec. 31; "Fluids in the Home," Saturday Jan. 2; "Heat in the Home," Tuesday, Jan. 5; "Electricity in the Home," Thursday, Jan. 7; "Light in the Home," Saturday, Jan. 9. The lecture hour is 3 o'clock.

Royal Society of Arts.—The Society's Session commenced on Wednesday, the 18th inst., with an Address from Sir Thomas Holdich, the Chairman of the Council of the Society. All the usual arrangements have been made for the Society's meetings, and the ordinary programme has been issued to the Fellows. Three of the papers to be read before Christmas deal with the chemical industries as affected by the war. The first of these is by Sir William Tilden, on "The Supply of Chemicals to Britain and her Dependencies," and the second by Dr. W. R. Ormandy on "Britain and Germany in Relation to the Chemical Trade." Sir William Ramsay will preside at the first of these and Lord Moulton at the second. The third paper is by Dr. Mollwo Perkin on "The Indian Indigo Industry," which has, of course, been very seriously affected by the production of synthetic indigo in Germany. The other two papers to be read before Christmas are not concerned with warlike matters—Sir William Abney, K.C.B., D.Sc., F.R.S., on "Permanent Pigments," and Mr. W. A. Young on "Metal work in the Eighteenth Century." In the same way a certain proportion of the papers announced for reading after Christmas refer to the effect of the war upon British trade, while others are concerned with the usual variety of topics proper to the Society's ordinary work.

The Sources of the World's Copper Supplies in 1913.—John B. C. Kershaw.—Since the commencement of the twentieth century nearly eight million tons of copper have been extracted from their ores, and have been consumed in the chief manufacturing countries of the world. The value of this metal, at an average price of £60 per ton for the whole period, is £480,000,000, or nearly two-thirds of our National Debt. How long can the earth continue to supply this enormous amount of copper, or to keep pace with the increasingly rapid growth in the demand for the red metal? It could certainly seem probable that within the lifetime of most of the readers of this article—or within the next twenty years—the "known" ore reserves of the existing mines will be worked out, and that unless new ore deposits of vast extent are discovered, copper will become one of the rarer and more costly metals before half the century is passed away. However, by that time some other metal or alloy will have been found to serve equally well the purposes for which copper is now used, and the disturbance and inconvenience caused by the rise in the price of copper in the marine and electrical engineering industries, will be reduced to a minimum by the change from copper to some other metal. Will this metal be aluminium?—*Engineering*, Oct. 16, 1914.

MEETINGS FOR THE WEEK.

MONDAY, 23rd.—Royal Society of Arts, 8. (Cantor Lecture). "The History and Practice of the Art of Printing," by R. A. Peckie.

Faraday Society, 8. General Discussion on "The Hardening of Metals."

WEDNESDAY, 25th.—Royal Society of Arts, 8. "The Supply of Chemicals to Great Britain and her Dependencies," by Sir William A. Tilden, F.R.S., &c.

FRIDAY, 27th.—Physical, 5. "Conduction of Electricity at Point Contacts," by A. F. Hallimond. "Thermal Conductivity of Badly-conducting Solids," by T. Barratt.

THE CHEMICAL NEWS.

VOL. CX., No. 2870.

THE FREEZING-POINT OF MILK.*

By J. BROWNLIE HENDERSON, F.I.C., and L. A. MESTON.

At the Australasian Association for the Advancement of Science Meeting in Brisbane in 1909, a paper was read by Mr. Henderson on "The Freezing-point of Milk; Its Use in the Detection of Added Water," and the paper was published in the printed *Proceedings* of that meeting.

So many inquiries were subsequently made for copies of the paper that the authors' copies have long since been exhausted, and it was thought advisable to put on record a more complete description of the work done on the subject at the Government Chemical Laboratory, Brisbane, and to record the results of the practical working of this process in a Foods Laboratory for over five years.

A short paper on the same subject by the same author was published in vol. xiii. of the *Australasian Association for the Advancement of Science*.

No article of food has caused more trouble to food analysts than milk, firstly, owing to the extremely important place it holds as an article of diet, and then owing to the great variations in its composition. Attempts to regulate the quality by fixing a minimum standard at once led to the watering down of rich milk to that low standard.

The legal standard for milk in Queensland is:—"Milk shall be the normal, clean, and fresh secretion obtained by completely emptying the udder of the healthy cow, properly fed and kept, excluding that got during fifteen days immediately before, and ten days immediately following on, parturition. It shall contain not less than eight and five-tenths per cent of milk solids not fat, three and three-tenths per cent of milk fat, and not less than twelve parts per cent of total solids; its freezing-point shall not be higher than 0.55°C . below zero."

This is a distinct advance on the old 8.5 solids not fat, and 3.0 per cent fat standard which almost invariably permitted the addition of at least 4.0 per cent of water without the mixture falling below the standard. The average of the milk supply of Brisbane is 8.9 per cent solids not fat, and 4.1 per cent of fat.

So far as we know this is the first occasion in the history of milk control that the freezing-point has actually been included in the legal minimum standard, though on the continent of Europe its use by food analysts in judging the quality of milk is by no means new. It is worthy of note that in Queensland there is no "appeal to the cow." The law provides not only that the milk shall be pure and clean and from healthy cows, but that it shall reach the above noted composition. Pure milk, which owing to its being derived from herds of unsuitable breed or from herds badly fed, falls below the prescribed standard may not be sold in Queensland.

In the paper above referred to it was pointed out that the attempts to solve the problem of added water in milk by treatment of the milk serum had all proved of little practical value. The refractive index method of which most was expected has been shown to be of little use. The index reading varies between 39 and 46, which means that a rich 46 milk might have nearly 20 per cent of water added to it ere falling below the 39 minimum. Apart from the manipulation difficulties, which are not small, the range of readings on genuine milk makes the process of little value.

Since E. Beckmann (*Milch Zeitung*, 1894) drew attention to the constancy of the freezing-point of milk, and

Winter in 1895 reported his work confirming it, the results of hundreds of thousands of analyses have added to the certainty of the position. The freezing-point of fresh milk from a herd of cows seems never to vary further than from -0.55°C . to -0.56°C . with a mean of -0.555°C . The maximum variation represents about 2 per cent of added water, while the working error of the process is less than 0.5 per cent of added water.

Before dealing with the details of the method, it might be well to note the reasons for the constancy of the freezing-point of a substance of such variable composition as milk.

The freezing-point of a solution of a substance in water depends mainly on the number of crystalloid ions dissolved in the solution.

Substances which are not in solution, like fat, do not affect the freezing-point. As fat is the most variable component of milk, the most varying factor is removed from affecting the result. Substances also which are in "colloid" solution such as the albumenoids affect the freezing-point either not at all or only to a very slight extent, and in any case as the molecular weight of the albumenoids is very high, their relative effect on the freezing-point is very small.

Thus the second most variable constituent of milk does not appreciably affect the result. The milk-sugar content of milk is fairly regular, but, again, we are dealing with a substance of high molecular weight and with a correspondingly small effect on the freezing-point.

It will thus be evident that we get down to the small proportion of other constituents ere we get the substances which control the freezing-point, and it seems that these, as in the blood of nearly all animals, are almost perfectly constant in proportion.

The freezing-point of milk is therefore not in any degree whatever a measure of the proportion of total solids or solids not fat present.

We have found milks of known genuine origin from small herds, with solids not fat 9.7 per cent and 7.6 per cent, as well as those of normal composition give exactly -0.555°C . freezing-point.

The following references to work done on the freezing-point of milk are worth noting:—

Dr. Barthel ("Methods used in the Examination of Milk and Dairy Products," 1910) refers to the freezing-point of milk as follows:—

"This method of determining the amount of added water is very simple and perfectly reliable if carried out carefully. It is remarkable that it has not found more general application, for it not only shows that water has been added, but gives also the amount with accuracy. The author has experimented with this method, and is quite satisfied that the results are reliable, and that in agreement with Winter and Parmentier, Schnorf, and others, pure unadulterated milk never has a higher freezing-point than -0.54°C . This is independent of breed, individuality, sexual excitement, the amount of fat, &c., but a very small addition of water at once raises the freezing-point."

J. Cornalba ("On the Milks of Lombardy," *Chem. Zeit.*, 1907-1909) shows the constancy of the freezing-point to fall between -0.55°C . and -0.56°C . He also points out that the colostrum with salts ranging between 0.9 per cent and 1.12 per cent gave normal freezing-points.

J. Winter and E. Parmentier obtained from single cows freezing-points varying from -0.54°C . to -0.57°C . The mixed milk from a herd never rose above -0.55°C . or fell below -0.56°C .

P. Ducross and H. Imbert (*Bull. Sciences Pharmacol.*, 1905) obtained a value of -0.533°C . from a sick cow, and a sample of milk from a cow in calf gave a freezing-point of -0.535°C .

Beckmann and Jordis ("Forschungs Berichte uber Lebensmittel," 1895, vol. ii.) found the average freezing-point to be -0.554°C .

* From the *Proceedings of the Royal Society*, Queensland, xxiv., 165.

It seems that for the mixed milk of a herd there is variation between only -0.55°C. and -0.56°C. , but for milk from single cows in a diseased or abnormal state wider variations may occur.

The freezing-point method places us in a sound position as regards the milk control. In the past, on the old standard, an honest milk vendor was liable to be prosecuted for selling as watered milk genuine milk which simply failed to reach the legal standard. On the freezing-point test, we have been able to warn three vendors in the last three years that the milk they were vending was genuine but below the legal standard, and that they had better take steps to improve their herds by feeding or "culling" in order to meet the standard.

It has been pointed out by one or two critics of the freezing-point method that the results can easily be masked by the addition of substances which depress the freezing-point.

Any of the substances likely to be used in this direction can be readily detected by an analyst. Many tests at the disposal of the analyst are liable to be masked, and it is part of his duty to look out for this masking, as, for example, the masking of the heat test of explosives by the addition of mercuric chloride, the masking of Becchi and Halphen reactions for cotton-seed oil by boiling the oil and other treatment, and the masking of Hehner's reaction for formaldehyde by adding sodium nitrite.

The freezing-point is such a sensitive test, however, that if the ordinary dairyman did start tampering with the milk he would either add too little to cover the addition of water or add too much and make the freezing-point abnormal.

For the last four years in the Government Chemical Laboratory, Brisbane, every legal sample of milk for prosecution purposes has been checked by this method, and most of the results are shown in Tables I., II., and III.

Table I. shows results obtained on legal samples of milk taken during the last three years, wherein an increased acidity had developed. When the milk becomes acid the larger molecules are decomposed into a number of smaller ones. The osmotic pressure increases, and the freezing-point is further depressed. Without this knowledge the results in Table I. would make it appear that some of the samples were abnormal before watering, while others were only slightly above the legal standard of 8.5 S.N.F. The added water, however (calculated on the minimum proportion of 0.5 per cent nitrogen and 0.7 per cent, ash found in normal milk), is higher than that estimated from the freezing-point of the sample.

We have not done sufficient work to enable us to say whether any definite relationship exists between the depression of the freezing-point and the increase of acidity. It is very doubtful if any constant factor could be obtained to correct for the acidity, as the fermentation products would vary with the nature of the ferment and the time and temperature of the reaction. Barthel states that the percentage of water can be determined fairly accurately if the acidity is 20° (Thorner) by adding 5 per cent to the result of Winter's formula. Figures obtained by us, on a small number of samples only, indicate that 1 per cent increase of acidity covers the addition of 0.5 per cent of water. It is to be noted that any error introduced by the increased acidity is entirely in favour of the milk vendor.

The acidity of milk is determined by Dr. Chapman's method, using 25 cc. of milk, 100 cc. of water, and 1 cc. of 0.1 per cent of phenolphthalein solution, and titrating with $n/10$ NaOH. The normal acidity of milk by this method is about 13.5 cc. $n/10$ NaOH per 100 cc. of milk.

TABLE II.—Showing Results from Legal Samples of Milk obtained during the last Three Years, containing 8.5 per Cent and over of Solids not Fat.

Total solids.	Fat.	Solids not fat.	Nitrogen.	Ash.	Freezing point.	Added H ₂ O calculated on f.p. -0.55°C. Per cent.
Per cent.	Per cent.	Percent.	Per cent.	Per cent.		
14.8	5.1	9.7		0.8	-0.555	
11.9	2.3	9.6		0.75	-0.550	
13.9	4.4	9.5		0.78	-0.555	
13.4	4.1	9.3		0.8	-0.555	
13.3	4.1	9.2			-0.561	
14.2	5.0	9.2			-0.550	
11.5	2.4	9.1	0.57	0.77	-0.550	
13.3	4.2	9.1			-0.555	
12.8	3.7	9.1			-0.543	1.2
14.2	5.2	9.0		0.71	-0.555	
14.1	5.1	9.0			-0.550	
14.4	5.4	9.0			-0.550	
13.1	4.1	9.0			-0.550	
12.4	3.4	9.0			-0.550	
13.5	4.5	9.0			-0.545	0.9
12.9	3.9	9.0			-0.545	0.9
12.8	3.8	9.0			-0.545	0.9
13.0	4.1	8.9			-0.557	
13.1	4.2	8.9			-0.557	
13.2	4.3	8.9			-0.543	1.2
12.9	4.0	8.9			-0.542	1.4
13.3	4.5	8.8			-0.560	
11.3	2.5	8.8	0.50	0.75	-0.550	
12.8	4.0	8.8			-0.550	
12.5	3.7	8.8			-0.550	
12.8	4.0	8.8			-0.544	1.0
13.3	4.5	8.8			-0.535	2.7
14.6	5.8	8.8			-0.523	4.8
13.6	4.8	8.8			-0.531	3.4
12.9	4.1	8.8			-0.520	5.4
12.6	3.9	8.7			-0.555	
13.3	4.6	8.7			-0.550	
12.4	3.7	8.7			-0.545	0.9
12.9	4.2	8.7			-0.540	1.8
13.3	4.6	8.7			-0.540	1.8
12.2	3.5	8.7			-0.510	7.2
12.6	4.0	8.6			-0.570	
12.4	3.8	8.6			-0.550	
13.2	4.6	8.6			-0.550	
12.2	3.6	8.6			-0.547	0.5
12.2	3.6	8.6			-0.547	0.5
11.7	3.1	8.6			-0.545	0.9
12.2	3.6	8.6			-0.532	3.2
12.3	3.7	8.6			-0.532	3.2
12.6	4.0	8.6			-0.530	3.6
11.3	2.8	8.5		0.72	-0.560	
11.5	3.0	8.5		0.71	-0.550	
12.2	3.7	8.5			-0.547	0.5
12.1	3.6	8.5			-0.544	1.0
11.7	3.2	8.5		0.69	-0.544	1.0
12.0	3.5	8.5			-0.542	1.4
12.4	3.9	8.5			-0.540	1.8
12.0	3.5	8.5		0.7	-0.540	1.8
12.6	4.1	8.5			-0.540	1.8
12.2	3.7	8.5			-0.535	2.7
12.1	3.6	8.5			-0.532	3.2
12.9	4.4	8.5			-0.530	3.6
12.5	4.0	8.5			-0.530	3.6
12.1	3.6	8.5			-0.530	3.6
12.4	3.9	8.5	0.47	0.7	-0.528	4.0
12.3	3.8	8.5		0.7	-0.527	4.1
12.3	3.8	8.5			-0.523	4.8
12.5	4.0	8.5		0.71	-0.520	5.4
12.6	4.1	8.5		0.74	-0.520	5.4

TABLE I.

Total solids.	Fat.	Solids not fat.	Nitro- gen.	Ash.	Acid. Cc. $n/10$ NaOH per 100 cc. milk.	Freezing point. $^{\circ}\text{C.}$	Added H ₂ O on 8.5 s.n.f.	Added H ₂ O on f.p.
Per cent.	Per cent.	Per cent.	Per cent.	Per cent.				
11.6	3.3	8.3	0.47	0.68	20.0	-0.540	2.3	1.8
12.4	4.2	8.2	0.47	0.66	18.4	-0.517	4.1	6.0
11.7	3.6	8.1	0.45	0.66	17.0	-0.537	4.7	2.3
12.2	4.1	8.1	0.46	0.68	15.6	-0.515	4.8	6.4
10.8	3.0	7.8	0.44	0.62	20.0	-0.500	8.3	9.1
10.6	3.0	7.6	0.42	0.63	24.0	-0.527	12.9	4.1
9.5	2.0	7.5	0.41	0.64	17.6	-0.520	11.8	5.4
8.8	2.5	6.3	0.36	0.50	17.6	-0.435	25.5	20.9

Summary of Table II.

Results from sixty-four legal samples of milk obtained during the last three years, containing from 8.5 to 9.7 per cent of solids not fat.

Number of samples.	Solids not fat. Per cent.	
6	9.2 to 9.7	All normal freezing-point.
3	9.1	Two normal freezing-point; one 1.2 per cent water.
8	9.0	Five normal freezing-point; three less than 1 per cent water.
4	8.9	Two normal freezing-point; two less than 1.5 per cent water.
9	8.8	Four normal freezing-point; five from 1 to 5.4 per cent water.
6	8.7	Three normal freezing-point; three from 2 to 7 per cent water.
9	8.6	Five normal freezing-point; four from 1 to 3.6 per cent water.
19	8.5	Three normal freezing-point; sixteen from 1 to 5.4 per cent water.

The amount of watering is not appreciable until the solids not fat figure falls below 8.9 per cent, although there are genuine milks on every figure from 8.5 to 8.9 per cent solids not fat. The greatest proportion of adulteration falls on the 8.5 figure—only three samples being genuine out of 19 received. The actual proportion of added water read off from Winter's table is given, as obviously for this comparison any working error of the process should not be taken into account.

(To be continued).

POTASH SALTS.

SUMMARY FOR 1913.*

Compiled by W. C. PHALEN, United States Geological Survey, Washington, D.C.

(Concluded from p. 252).

Shipments from German Potash Mines.

FROM data obtained from reliable sources the following table, showing the shipments of potash salts and potash fertilisers, in metric tons, from the German potash mines, for native and foreign consumption, during the last two years, has been compiled:—

Shipments of Potash Salts from German Mines in 1911 and 1912.

Potash salts.	1911.	1912.
Muriate of potash	443,357	471,435
Sulphate of potassium	110,123	115,728
Magnesium, 48 per cent K ₂ O	49,014	55,987
Magnesium, 40 per cent K ₂ O	144	173
Manure salts—		
Minimum, 38 per cent K ₂ O	38,620	48,059
Minimum, 20 per cent K ₂ O	169,812	174,867
Minimum, 30 per cent K ₂ O	57,502	64,514
Minimum, 40 per cent K ₂ O	379,790	483,877
Kainit and sylvinit	3,312,632	3,251,003
Carnallite, &c.	80,660	70,462
Total	4,641,654	4,736,105

Changes have been made in the method of preparing the statistics for 1912, so as to preclude comparison in all cases between shipments of that year with 1911.

Table II. shows the exports of German potash salts

* From *The Chemical Engineer*, xx., No. 3.

TABLE V.—Fertilisers Imported and Entered for Consumption in the United States, 1909—1913, in Long Tons.

	1913.		1912.		1911.		1910.		1909.	
	Quantity.	Value (dols.).	Quantity.	Value (dols.).	Quantity.	Value (dols.).	Quantity.	Value (dols.).	Quantity.	Value (dols.).
Apatite	35,012	851,136	26,729	1,410,248	36,856	943,472	48,979	1,140,476	2,925	19,013
Bone-dust (or animal carbon) and bone ash, fit only for fertilising purposes	16,674	518,429	19,128	329,624	5,292	292,496	33,565	667,870	29,035	685,291
Calcium cyanamide or lime nitrogen	465,336	2,201,730	511,076	2,386,362	563,957	2,748,140	582,197	2,798,198	(a)	(a)
Guano	223,687	2,245,509	171,757	1,797,057	159,796	1,660,040	147,242	1,013,000	44,197	772,674
Kainit	17,121	124,815	28,821	231,255	16,153	157,394	21,706	23,040	163,943	854,998
Manure salts, including double manure salts	13,186	130,455	12,596	114,300	12,622	87,994	10,774	93,650	52,958	601,804
Phosphates, crude	154,729	3,314,460	127,932	2,660,887	197,810	4,098,321	195,991	3,394,279	9,983	99,060
Slag, basic, ground or unground	955,436	10,819,253	999,338	8,893,090	1,029,375	10,762,472	1,043,994	9,520,074	690	5,880
All other substances used only for manure									184,850	2,879,845
Total									488,581	5,918,565

(a) Not separately classified.

(b) From August 5 to December 31.

TABLE II.—Exports of German Potash Salts in 1911 and 1912.

Potash salts.	1911.		1912.	
	Total.	To United States.	Total.	To United States.
Muriate of potash.	329,751	229,431	286,528	190,775
Sulphate of potassium.	109,529	56,893	85,452	35,366
Sulphate of potassium-magnesium	282,574 (a)	143,775 (a)	48,540	14,172
Carnallite, with at least 9 per cent and less than 12 per cent K ₂ O			6,853	(b)
Raw potash salts, with from 12 to 15 per cent K ₂ O			852,984	461,279
Raw potash salts, with more than 15 per cent and less than 20 per cent K ₂ O	1,167,972 (c)			
Manure salts, including potash salts with 38 per cent K ₂ O			35,529	29,533
Abraum salts, Stassfurter salts, &c.			373,665	149,907
			31,322	9,578
Total	1,889,826		1,720,837	890,610

(a) Includes manure salts.

(b) Not stated.

(c) Only the total exports of the last five salts for the

year 1911 are given in the new statistics, and the shipments to the United States during that year are not specified.

TABLE III.—Potash Salts Imported into United States for the Calendar Years 1910-1913, in Pounds. (a)

Potash.	1910.		1911.		1912.		1913.	
	Quantity.	Value (dols.).	Quantity.	Value (dols.).	Quantity.	Value (dols.).	Quantity.	Value (dols.).
Carbonate of	18,963,619	616,371	20,332,990	636,356	20,530,846	658,343	21,436,533	652,635
Caustic, not including ref.	8,304,696	346,388	7,069,837	287,116	9,578,437	365,860	8,590,120	335,147
Cyanide of (b)	—	—	(d) 2,114,684	(d) 316,027	1,138,569	169,627	1,023,167	143,999
Chloride of	381,873,875	5,252,373	509,119,193	7,651,684	482,265,665	7,229,109	478,826,857	7,120,055
Nitrate of (or salt-petre), crude	11,496,904	333,854	7,945,747	265,061	7,315,531	216,492	9,876,910	262,575
Sulphate of	86,162,874	1,426,975	121,039,192	2,227,820	97,161,010	1,769,676	88,565,073	1,633,114
All other (c)	3,389,684	387,662	4,583,940	442,042	3,509,444	316,989	6,114,748	554,637
Total	510,191,652	8,363,623	672,205,583	11,826,106	621,499,502	10,726,096	614,433,408	10,702,162

(a) This table is based on total imports for the calendar year, not, as some tables, on imports for consumption for the calendar year.

(b) Included in "All other chemicals" prior to July 1, 1911.

(c) Included in "All other chemicals" prior to July 1, 1909.

(d) Figures cover period since July 1.

TABLE IV.—Potash Salts Imported for Consumption into the United States for the Calendar Years 1911-1913, in Pounds.

Potash.	1911.		1912.		1913.	
	Quantity.	Value (dols.).	Quantity.	Value (dols.).	Quantity.	Value (dols.).
Carbonate of, crude	8,604,855	255,096	7,625,382	234,868	9,715,878	272,973
Caustic, not including refined	7,072,093	287,097	9,690,494	370,506	8,648,753 (a)	342,056
Cyanide of	2,649,040	294,141	726,659	109,434	1,395,987	205,037
Chloride of	506,570,661	7,651,693	482,529,396	7,229,121	475,261,595	7,075,745
Nitrate of (salt-petre), crude	7,944,757	265,061	6,511,208	202,899	9,652,366	261,078
Sulphate of	121,710,568	2,240,631	98,237,150	1,783,846	88,698,193	1,677,429
All other	15,570,411	689,662	16,858,875	761,611	19,067,144	959,595
Total	670,122,385	11,783,381	622,179,164	10,692,285	612,439,916	10,793,913

(a) Including refined.

for 1911 and 1912 and the amount shipped to the United States, in metric tons, with comparisons where possible.

Consumption of Potash Salts in the United States.

Table III. gives the total imports of potash salts in pounds for the years 1910 to 1913, inclusive.

For comparison Table IV. is added. This gives the potash salts imported for consumption into the United States during the calendar years 1911, 1912, and 1913, in pounds.

It will be observed that there was a slight decrease in both quantity and value of potash salts imported in 1913 as compared with 1912. The quantities of carbonate,

cyanide, nitrate, and "all other salts" of potassium increased, while the quantity of caustic potash, chloride, and sulphate diminished. The results, especially in the case of the two latter salts, are of interest, for among the potassium salts imported it is presumably these two that enter most largely into the commercial fertiliser industry.

The importation of potash salts given in these tables is only a part of that entering the United States from Germany. To it should be added the importation of kainit and manure salts. The quantity and value of imported fertilisers, included kainit and manure salts, are given in detail in Table V. It indicates a growing and prosperous industry.

AIR OZONATION.*

By MILTON W. FRANKLIN.

(Concluded from p. 254).

III. Cold Storage and Food Preservation.

CZAPLEWSKI states—

"A great field for ozone ventilation seems to open in the food industry, especially in the cold storage chambers of abattoirs. Ozone has been shown to have caused direct saving in many of these plants, the meat remaining fresh and sweet for a much longer period with ozone than without. In egg cold storage the ozone has given excellent results in that the disagreeable straw and box odours disappear, the eggs last longer, and fewer decay."

Bail (*Prog. Med. Wochenschr.*, 1913, No. 17, p. 217) reports, referring to the Cologne abattoir—

"Meat that had decayed was at least partially reclaimed by the ozone, the mould coating having disappeared."

Saint Pére (*Revue Generale de Froid*, March, 1912, No. 34) states—

"Only pure ozone should be used in food preservation. Pure ozone on decomposition yields only pure oxygen, but this is not true of ozone contaminated with other gases. The latter gives a peculiar odour to eggs, meats, &c., due to the nitrogen oxide impurities. The odour fixes itself permanently in the moist parts of meats, as the muscular fibres, ruining the best qualities. This contamination in ozone does not harmfully affect fruits; the thickness of the skin is apparently effectively increased, thus protecting it against the cold which otherwise hinders ripening."

For most varieties of foods there exists a certain critical temperature below which they may not be stored without injurious freezing and above which they are liable to deleterious bacterial invasion. It is extremely difficult to maintain rooms at the right temperature owing to the constant entrance and exit of operatives and because masses of material to be stored diffuse great quantities of heat on cooling down. The function of ozone is to limit bacterial activity at temperatures at which they might otherwise thrive.

Egg Storage.—We have performed experiments with the preservation of eggs at ordinary temperatures and present the results herewith—

Preliminary tests were made to determine the effect of ozone on egg albumin and to note the effect of vacua on eggs. The eggs in all of the tests were from white Leghorn hens and were laid in the morning of the day of the tests.

The albumin of three eggs was well mixed, diluted with an equal quantity of water and divided into two parts. One part was put into a Petri dish, 6 inches in diameter and $\frac{3}{4}$ inch deep, and placed under a bell-jar (9 inches in diameter by 12 inches high), with openings at the top and near the bottom at the side. Glass tubes provided with stopcocks were inserted through corks in these openings, the one passing through the top opening extending downward inside the bell-jar almost to the Petri dish. The lower glass tube was connected to an aspirator and ozonised air containing 5 grms. per cbm. was drawn from the upper tube over the Petri dish at the rate of 1 cbm. per hour. The total amount of air was 170 l., ozone 850 mgrms., period ten minutes.

The albumin coagulated considerably, and the whole mass turned a weak yellowish grey colour which was distinctly noticeable but not pronounced. There was no odour of ozone in the resulting coagulum. Straining and weighing showed that the coagulum represented 27.4 per cent of the total albumin.

The remaining half of the albumin solution was treated in the same way with atmospheric air instead of ozonised air. The amount of air and the period were the same, and there was 16.4 per cent coagulation but no discoloration.

Ten eggs were weighed, numbered, and placed under the bell-jar in a Petri dish. The jar was then evacuated to 0.46 mm. hg. and kept in this state for two hours, when the pressure had risen 2.37 mm. owing to evaporation from the eggs, none having broken. The air was then slowly introduced till atmospheric pressure was reached and the eggs removed and weighed.

Weight.	1.	2.	3.	4.	5.
G.	57.13	63.06	68.75	61.78	61.61
Loss, per cent.	0.402	0.365	0.465	0.461	0.372
Weight.	6.	7.	8.	9.	10.
G.	62.62	54.79	57.23	53.80	57.43
Loss, per cent.	0.335	0.381	0.540	0.473	0.400

Mean weight before 59.82 grms.

Mean weight after 59.57 grms.

Mean loss, grm. 0.25

Mean loss, per cent 0.42

These eggs were among the checks in the following experiments:—Ten salt mouth bottles of 1 l. capacity were fitted with corks $\frac{1}{2}$ inch thick, boiled in paraffin and provided with two glass tubes with stopcocks. Two eggs, weighed and numbered, were placed in each bottle and the corks replaced and sealed with paraffin. The bottles were exhausted to 0.59 mm. hg., after which air containing 320 mgrms. ozone per cbm. was slowly introduced. Ten control bottles were prepared in precisely the same way, with the exception that the air contained no ozone, and furnished with eggs. The bottles were numbered and put away in a dark room and at periods of ten days one ozonised bottle and one check bottle were opened and the eggs examined and compared. One egg from each bottle was boiled and the other fried in Crisco, and wherever possible all of the eggs were eaten. The temperature varied from 16° C. to 25° C. during the whole period.

Ten days.—There was no ozone left in the bottle. Both eggs were all right in every respect; loss of weight, 0.10 per cent and 0.17 per cent.

The control eggs were all right; loss of weight 0.19 per cent and 0.24 per cent.

The remaining bottles were then evacuated and ozonised as at the beginning of the test and the control bottles evacuated and filled with air. In two bottles the eggs cracked and were discarded.

Twenty days.—The ozonised eggs were all right in every respect; loss in weight, 0.45 per cent and 0.49 per cent; no ozone left.

Of the unozonised eggs the boiled one tasted like an old storage egg, but the fried one seemed all right; the bottle had no smell; loss in weight, 0.57 per cent and 0.56 per cent.

Thirty days.—The ozonised eggs looked, smelled, and tasted all right; no ozone left; spot in both shells because eggs had not been turned; loss in weight, 0.84 per cent and 0.55 per cent.

The unozonised bottle smelt from mildew; eggs looked weedy and spoiled; neither could be eaten; half of the inside of shell was black from lack of turning; loss in weight, 0.72 per cent and 0.75 per cent.

Forty days.—Ozonised eggs both good in all respects; loss in weight, 0.65 per cent and 0.98 per cent; no ozone left.

The unozonised bottle smelt from mildew; both eggs thoroughly bad; could not be eaten; loss in weight, 0.88 per cent and 0.96 per cent.

Fifty days.—Ozonised eggs both all right in all respects; no ozone; loss in weight, 1.25 per cent and 1.12 per cent.

Unozonised eggs essentially same as at forty days.

Sixty days.—Ozonised bottle showed slight trace of mildew; shells slightly mildewed; eggs both eaten but did not seem altogether fresh; loss in weight, 1.65 per cent and 1.52 per cent.

Unozonised eggs essentially as in forty and sixty day

* From *Journal of Industrial and Engineering Chemistry*, vi., No. 10.

test but more pronounced; loss in weight, 1.38 per cent and 1.76 per cent.

Seventy days.—Smell of mildew in ozone bottle; boiled egg could not be eaten but fried egg was eaten and tasted somewhat stale; loss in weight, 1.59 per cent and 1.69 per cent.

Unozonised eggs were thoroughly rotten and mildewed; strong H₂S odour.

It should be noted that the corks were not tight after the first trial; the ozone disappeared in a short time, the period lessening after each treatment; the ozonised eggs lasted about twice as long as the unozonised eggs; the temperatures were very high throughout. Further test with ozone supplied constantly are to be reported later.

Fresh eggs are covered with a thin mucilaginous envelope which renders them air-tight, but after a time this dries and desquamates, leaving the porous shell unprotected. Then follows a period during which evaporation takes place and much of the water of the egg passes through the shell, being replaced by air from without. This air carries a variety of enzymes and other micro-organisms through to the interior of the egg, and it is probable that all the putrefactive changes in the egg are due to the activity of these organisms because the contents of fresh eggs are known to be absolutely sterile. Ozone by lessening the number and activity of these organisms inhibits the putrefactive processes to which stored eggs are otherwise liable.

Conclusions.

From the evidence presented above, the following conclusions may be drawn:—

I. Ozone destroys the odour of certain foodstuffs and other organic sources of odour.

II. Ozone is in no sense poisonous, though in great concentrations it is capable of causing local irritation of the mucous membranes with which it comes in contact.

III. Prolonged ozonisation is capable of ridding, at least in a measure, the atmosphere of food storage rooms of germ life, probably through rendering it an unsuitable medium for their support.

IV. Ozone is a valuable adjunct to ventilation, its function being the destruction of odour with consequent partial purification of the air; there is nothing either in the theory or in recorded experience to warrant its use for curtailing ventilation.

V. Eggs may be preserved longer with the aid of ozone than under similar conditions without.

VI. The analogy between laboratory tests and actual practical applications is often so obscure and replete with modifying factors that the extremest care must be exercised in applying the results of experimental observations to practice.

Christmas Cards.—We suppose there is nobody in these days who believes that Berlin wool comes from Berlin, otherwise there would be but small chance of our soldiers getting knitted comforts this winter. Why, then, do the British public still persist in thinking that all Christmas cards come from Germany? They may have at one time, but for the last twenty years the manufacture of Christmas cards has been a growing British industry, and now all the best are made in England. The business is one of vast extent, employing thousands of men and women. The private Christmas cards is absolutely a British industry, and we hope that the public will buy as usual, and thus keep up the cheery custom, particularly at a time when everyone wants good wishes more than ever. By so doing they will keep a vast number of people in work, which is a matter of great importance at such a time as this.

RADIUM.*

MR. FOSTER, from the Committee on Mines and Mining, submitted the following

REPORT.

The Committee on Mines and Mining, to which was referred H. J. Res. 185, introduced by Mr. Foster; H. J. Res. 186, introduced by Mr. Ferris; H. R. 12,112, introduced by Mr. Mondell; and H. R. 12,741, introduced by Mr. Foster, each having the same general purpose of securing an adequate supply of radium for the use of the Government and people of the United States, begs leave to report H. R. 12,741 without amendment, and recommends the Bill for passage.

Hearings.

Upon the reference of the Resolutions and Bills to this Committee, we began on January 19, 1914, to hold public hearings for the purpose of obtaining information on the subject from those in favour, as well as from those opposed. The Committee gave six days to the hearings, and gave full opportunity for those interested to appear and testify. As a result of these hearings, the Committee reports back H. R. 12,741, with the recommendation that it be passed:—

A Bill to provide for and encourage the prospecting, mining, and treatment of radium-bearing ores in lands belonging to the United States, for the purpose of securing an adequate supply of radium for Government and other hospitals in the United States, and for other purposes.

Be it enacted by the Senate and House of Representatives of the United States of America in Congress assembled, That all deposits of carnotite, pitchblende, or other ores, containing radium in sufficient quantity for extraction, in lands belonging to the United States, and the lands containing same, shall be subject to exploration, occupation, and purchase under the mining laws upon condition that said radium-bearing ores shall be exclusively sold and delivered to the United States as hereinafter provided, and all said ores hereafter mined from lands the title to which is now in the United States, and which were not located under the mining laws of the United States, and of the States wherein the same are situated prior to January 15, 1914, shall be so sold and delivered, and the exclusive right of the United States to purchase and receive said ores from the owners of such lands, their lessees and assigns, together with the right of the United States to annul and void any patent issued for such lands because of failure to develop and mine such ores with reasonable diligence, shall be expressly reserved in any and all patents which may hereafter be issued.

SEC. 2. That the locators of lands containing said deposits of radium-bearing ores shall prospect, mine, and develop such deposits continuously and in good faith, and failure to prosecute such prospecting, mining, and development on lands chiefly valuable for said deposits for a consecutive period of four months in any calendar year shall subject the same to relocation, or, in the absence of relocation, to forfeiture at the discretion of the Secretary of the Interior: *Provided*, That the Secretary of the Interior shall have authority by public notice to suspend for such period as he may fix the requirement of continuous development as hereinbefore provided.

SEC. 3. That the sale, gift, or other disposition of said radium-bearing ores to any person, association, or corporation other than the United States shall be unlawful, and any violation hereof shall subject any location made or patent issued to forfeiture, and the person, association, or corporation so selling, giving, or otherwise unlawfully disposing of said ores shall, upon conviction thereof, be punished by a fine of not less than twice the value of the

* Report No. 214, presented to the House of Representatives, U.S.A., at the 63rd Congress.

nores so sold, given away, or unlawfully disposed of *Provided*, That when in the opinion of the Secretary of the Interior special conditions arise which may make such action necessary he may, by special order, permit the sale and delivery of said ores after or without tender to the United States, as he may deem advisable.

SEC. 4. That the Secretary of the Interior be, and he is hereby, authorised to erect, maintain, and operate a plant or plants for the concentration and treatment of radium-bearing ores and the extraction of the radium and by-products therefrom; to purchase radium-bearing ores mined from lands occupied and held under the provisions of this Act at such prices to be fixed by him from time to time and published in advance on the first day of January and of July in each year, as will insure the prospecting for and mining of such ores, and, if need arises, to purchase or accept radium-bearing ores from other sources; to sell the by-products of such ores at the best prices obtainable; and he shall make such disposition or use of the radium produced as will best serve the needs of the people of the United States.

SEC. 5. That the Secretary of the Interior shall report to Congress at the beginning of each regular session all receipts, expenditures, and operations under the provisions of this Act, with such recommendations concerning future operations as he shall deem proper. All mining operations on lands located as herein provided for shall at all times be subject to inspection by authorised representatives of the Secretary of the Interior, and the locators or patentees of such lands, their lessees and assigns, shall transmit monthly to the Secretary of the Interior or to his authorised representative a statement of all developments, the nature thereof, and the quantity of ore mined.

SEC. 6. That there is hereby authorised for the erection and general equipment of a suitable building or buildings for the radium extraction and other work of the Bureau of Mines in the metal-mining States the sum of 150,000 dols., and for the necessary expenses connected with the purchase and treatment of radium-bearing ores and the extraction of radium therefrom during the fiscal year ending June 30, 1915, the further sum of 300,000 dols.

General Scope of the Bill.

The Bill as reported withdraws no land from entry, nor does it reserve to the United States the ownership of radium-carrying ore deposits on lands still under Government control. It simply gives to the General Government a preferential right to purchase the radium-bearing ores from lands now owned by the Government, at such prices to be fixed by the Secretary of the Interior as will cover the cost of and encourage mining operations, and under conditions that require the full and prompt development of the radium deposits for the benefit of the people. At the same time it furnishes to the actual prospector or miner a steady market for his ores and sure and prompt payment for the material when sold—two conditions that he has not always enjoyed in the past.

The purpose of this Bill is therefore correctly reported:—

To provide for and encourage the prospecting, mining, and treatment of radium-bearing ores in lands belonging to the United States, for the purpose of securing an adequate supply of radium for Government and other hospitals in the United States, and for other purposes.

The Bill safeguards the interests of all the people, and provides for any unforeseen conditions by authorising the Secretary of the Interior to fix semiannually the price to be paid for the ores under conditions that will ensure the prospecting for and mining of them; allows the Secretary to permit the sale and delivery of these ores after or without tender to the United States, if conditions arise which make this advisable, *i.e.*, if conditions arise under which the Government is for a time unprepared to purchase the ores; and it permits him to accept or purchase radium-bearing ores from deposits already in the hands of private

individuals, should such tenders be made and the material be needed. It also authorises him to dispose of the radium extracted under conditions that will best serve the needs of the people of the United States, keeping in mind always the needs of the many who are unable to bear the burden of expensive journeys or costly treatment which now limit such treatment to the few. It authorises an appropriation to cover the cost of the mining of the radium-bearing ores on the public lands and the extraction of the radium. If such policy is deemed wise, the Secretary of the Interior may sell a part or all of the radium produced to American hospitals at cost of production, and turn the receipts therefrom into the Treasury, thus reimbursing the Government in part or in full for the expenditures under this Act.

General Summary.

From information brought before it the Committee is convinced of the great public need of the legislation herein proposed. It has been shown by the highest medical authority and to the Committee's satisfaction that radium is a cure for certain forms of cancer, particularly those of an external nature which have not progressed beyond the reach of this or any other remedy; that it is almost a specific in certain forms of giant sarcoma; and that many cases of cancer quite beyond the hope of surgery can be and have been cured by this agent. From the evidence at hand it seems probable that by the use of larger quantities of radium than are now available a large number of present failures might be transformed into cures. Unfortunately up to the present time no American surgeon has been able to procure for use in any case more than 1 grm. of radium—a quantity not larger than a garden pea—and the total quantity now available for all American hospitals does not exceed 2 grms.

As there are estimated to be over 200,000 cases of cancer in the United States, and 75,000 people yearly are said to die of cancer, the importance of this discovery, and the seriousness of this situation for the American people, cannot be over-estimated. It has been shown to the satisfaction of the Committee that during the last two or three years the United States has supplied from two to three times as much of the raw material used in producing radium as all the rest of the world together; that this material has for the main part been exported to foreign countries at prices entirely incommensurate with the actual value of the contained radium; that up to January 1, 1914, only 2 grms. of this material had been produced in the United States, and that one company—the only company in the United States now actually producing and selling this material—has already contracted abroad for the major part of its 1914 output. It has also been shown that, on account of the great foreign demand for the material, it is practically impossible to procure radium at any price for immediate delivery, and that when future deliveries are promised the price is so high and so far beyond the actual cost of production that there is small hope that this remedy will become generally available for rich and poor alike in this country.

Your Committee is therefore convinced that Congress should immediately take steps, as proposed in this Bill, to develop the radium resources still belonging to the people of this country, and to do this under conditions that will secure and make immediately and widely available the largest possible supply of this radium for the treatment of the sufferers from cancer among the people in the United States. The Bill now reported will accomplish this purpose in a manner which, it is believed, instead of discouraging will encourage and stimulate the prospector to discover and mine the radium ore deposits by giving him a certain and fair reward for his discovery and his work.

Discovery of Radium.

In 1896 Prof. Henry Becquerel, in France, in some experiments that he was conducting in connection with the ability of substances, rendered phosphorescent under the

influence of Röntgen rays, to photograph themselves, made the interesting discovery that uranium and its salts possess to a small degree the property of giving off rays that affect a photographic plate through material ordinarily opaque, as the X-ray was known to do. As a result of this experiment Prof. P. and M^{me}. S. Curie conceived the idea that these rays must come from some new element, and undertook to separate this element from the ores from which uranium had been produced, as certain of these ores were found to be more radioactive than uranium.

In 1898 Prof. and M^{me}. Curie succeeded in obtaining from certain residues of uranium manufactured in Austria a new element which they announced under the name of "radium." This material was found to possess the property of giving off amounts of energy far in excess of any previously known material, and the extended investigations undertaken since have greatly augmented the knowledge of the subject. Details of the investigations can be found in a classic work on the subject, entitled "Radioactive Substances and Their Radiations," by E. Rutherford, University of Manchester, England.

During the early years of the study of radium certain pitchblende residues that can no longer be obtained were available, and these were more radioactive than the ore itself. Dr. Giesel, chemist of the Chinin Fabrique, Brunswick, Germany, interested himself in procuring enough of the material to supply certain scientists with it at cost, so that its properties might be investigated. Some of these early workers obtained radium at less than 20 dols. a mgrm.; from this figure the price of the material has steadily risen until to-day the quoted price for future delivery is 120 dols. per mgrm. in radium bromide of 60 per cent. purity. In pure radium bromide, which, however, is not necessary for most purposes, the price of radium metal is approximately 180 dols. per mgrm. (120 dols. per mgrm. is equivalent to 3,400,000 dols. per ounce average).

It should be remembered, also, that the total amount of radium extracted up to the present time is probably not in excess of an ounce of radium metal.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 12, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"Analyses of Agricultural Yield. Part I. Spacing Experiments with Egyptian Cotton." By W. L. BALLS and F. S. HOLTON.

The aim of the experiments is the statistical analysis of the yield of agricultural crops, in terms of plant development, by careful recording of all stages. The effects of environmental conditions on crop development can then be satisfactorily analysed.

The effects of varying spacing, date of sowing, and season, upon Egyptian cotton, have been subjected in this way to critical examination by the authors. A secondary aim has been to appreciate the reasons for conventional agricultural practice.

For each of twenty different spacings, the numbers of flowers daily, and of fruits, together with the weights of cotton and seed per fruit, have been recorded. The extent to which each of these components enters into the building up of the final yield is shown. The statistics provide a body of data free from subjective bias, from which trustworthy conclusions can be drawn. Such data can be computed and plotted graphically day by day throughout

the season, so that the life history of the crop and the building of its yield may be presented in the form of plant-development curves.

The dense planting conventionally practised by the Egyptian fellah is shown to give the maximum possible yield per unit area under the limitations of field cultivation, though the normal extension of the root-system of an isolated plant can utilise more than ten times the soil-surface allotted to it in field-crop. Most of the phenomena of field-crop physiology in the fruiting season are thus shown to be traceable to root-interference.

"Fixation of Arsenic by the Brain after Intravenous Injections of Salvarsan." By J. MCINTOSH and P. FILDES. After intravenous injections of salvarsan and neosalvarsan in man and animals no arsenic can be found in the brain.

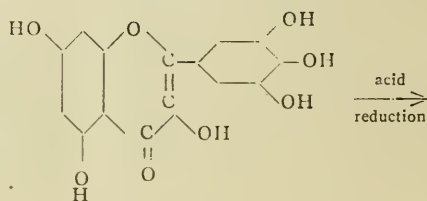
This phenomenon is not due to lack of affinity between the brain and the drugs, but to an inability on the part of the drugs to penetrate into the substance of the brain.

Fixation of arsenic by the brain occurs as readily as by the liver, as shown by experiments *in vitro* and the toxic effects of intrathecal injections.

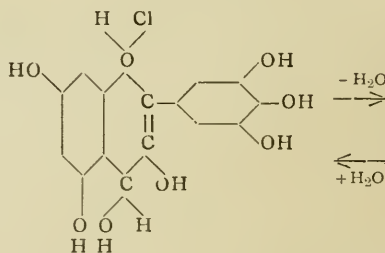
Penetration of neosalvarsan into the brain cannot be obtained even by frequently repeated intravenous injections.

"Production of Anthocyanins and Anthocyanidins." (Part II.). By A. E. EVEREST.

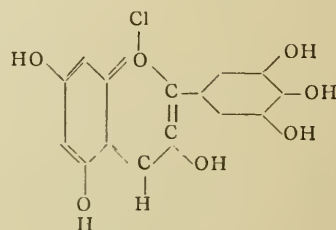
The author brings forward further evidence to support the conclusions arrived at by him in his previous paper (*Roy. Soc. Proc.*, 1914, B, lxxxvii., 144), namely, that the red, blue, and violet flower and fruit pigments (Anthocyanins) may be produced by reduction of flavone and flavonal derivatives in acid solution, according to the scheme:—



I.
Flavonol derivative.



II.
Colourless or faintly coloured intermediate product.



III.
Anthocyanin pigment.

and that the structural formulæ of such anthocyanins are of the type III.

Experiments are described which show that pure

disaccharides of the flavonol series pass without hydrolysis to anthocyanins.

The flavone and flavonol pigments having been previously synthesised by Kostanecki, the processes described by the author complete the synthesis of the anthocyan pigments.

Criticisms of the author's results by other workers are answered and shown to be unsound.

"*Living Observations on the Life-cycle of a New Flagellate Helkesimastix faecicola: together with Remarks on the Question of Syngamy in the Trypanosomes.*" By H. M. WOODCOCK and G. LAPAGE.

Helkesimastix faecicola n.g., n.sp., occurs in goat dung and sheep-dung; it is a "passenger," being carried through the alimentary canal in an encysted state. We have cultivated this flagellate in various media.

We have observed the entire course of the life-cycle in life, from excystation to encystment. The active form is remarkable in possessing only a single flagellum, which corresponds to the trailing flagellum of a *Bodo* or a *Cercomonas* (*Cercobodo*). The flagellum is closely applied to the body, but no definite membrane is developed.

Syngamy is very general, and the early behaviour of a conjugating pair is remarkable, owing to the very plastic nature of the cytoplasm. Encystment is invariably the direct sequel to syngamy.

Intensive culture of this flagellate has resulted in the production of a strain which is no longer able to undergo true syngamy and to form cysts. The existence of this "aconjugating" strain is now dependent on further transferences to fresh medium.

This experimental observation has an important bearing on the question of syngamy in the trypanosomes and allied parasitic flagellates. These have in all probability lost the power to conjugate. The conditions of life in their case may be compared to those of the above mentioned intensive culture of *Helkesimastix*. We consider that the loss of syngamy in such forms is due to a surfeit of nutrition, together with the removal of an excess of toxic products from the environment.

"*Antagonistic Action of Carbon Dioxide and Adrenalin on the Heart.*" By S. W. PATTERSON.

Carbon dioxide alone depresses all the functions of the isolated heart.

Adrenalin besides dilating the coronary vessels has a specific action in increasing the rate and strength of ventricular contraction.

The effect of carbon dioxide and adrenalin combined is still to allow of more rapid and stronger contraction and rapid relaxation, and also to lengthen the diastolic period. Thus, greater filling of the heart takes place, and the heart is in a better condition for putting out a maximal output.

CHEMICAL SOCIETY.

The following are abstracts of papers received during the vacation, and published, or passed for publication, in the *Transactions* :—

197. "*Interaction of Alkali Alkyl Sulphates and Alkali Nitrites: Theories of the Formation of Aliphatic Nitro-compounds.*" By PANCHANON NEOGI. (*Trans.*, 1914, 2371).

Aliphatic nitrites and nitro-compounds have been prepared by the interaction of the alkali salts of methyl-, propyl-, isobutyl-, and isoamyl-sulphuric acids and sodium, potassium, calcium, and barium nitrites. The theory of tautomerism is discussed, and two new theories, namely, those of "isomeric conversion" and "additive combination," are advanced.

198. "*The Influence of Acids and Alkalis on the Optical Activity of some Amino-acids.*" By JOHN KERFOOT WOOD. (*Trans.*, 1914, 1988).

The author has determined the optical activity of leucine,

aspartic acid, and glutamic acid in aqueous solution and in the presence of varying amounts of hydrochloric acid and of sodium hydroxide. It is shown how it is possible to calculate from the results of the experiments the degree of hydrolysis of the salts of the amino-acids, and the basic and acidic ionisation-constants of the latter. The values obtained for the basic ionisation constants of leucine and aspartic acid are in very close agreement with those arrived at by other methods.

199. "*The Velocities of Flame in Mixtures of Methane and Air.*" By ALBERT PARKER and ALAN VICTOR RHEAD. (*Trans.*, 1914, 2150).

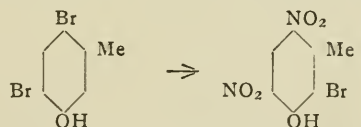
The velocities of the flame of mixtures of methane and air in different proportions have been determined at different points in 2.5 cm. tubes of glass, copper, iron, and lead. Thin strips of Wood's alloy (melting at 72°) stretched across the tubes at various points were used as flame indicators. The metal bridges were placed in electrical connection with a magnet, which operated a stylus on a revolving drum. It has been found that the propagation of flame in mixtures of methane and air occurs in three distinct periods when fired from an open to a closed end of a tube. In the first period the flame travels with a constant and uniform velocity. The second period consists of vibratory movements and a sudden increase in velocity. In the third period the rate again falls to a uniform value as the flame approaches the closed end.

In tubes of the same diameter the initial velocity of explosion varies with the material of the tube; the velocity is less in tubes possessing a higher conductivity for heat.

The most explosive mixture, which contains 10 per cent of methane, possesses an initial velocity of 70 cm. per second. The velocity decreases with change of the amount of methane present, moving towards zero at 4.5 and 13.1 per cent. The effect of a bend in the explosion tube has been found to vary with the percentage composition of the mixture.

200. "*Experiments on the Migration of Para-halogen Atoms in Phenols.*" By IVAN RICHARD GIBBS and PHILIP WILFRED ROBERTSON. (*Trans.*, 1914, 1885).

The authors have studied the action of nitric acid on certain *p*-bromo-*m*-cresols in which one of the ortho-positions is free. In only one instance was the migration of bromine observed, namely, in the case of 4:6-dibromo-*m*-cresol, which yielded on nitration the 2-bromo-4:6-dinitro-derivative :—



201. "*Some Derivatives of Safrrole.*" By ROBINSON PERCY FOULDS and ROBERT ROBINSON. (*Trans.*, 1914, 1963).

6-Nitrosafrole was prepared, and found to be readily reduced to 6-aminasafrole, the acetyl derivative of which could be changed to either a quinoline or an indole derivative. 6-Nitrosafrole, on oxidation with permanganate, yielded 6-nitropiperonylacetic acid, which could not be further oxidised to a nitropiperonylic acid.

202. "*Position-isomerism and Optical Activity.*" By JULIUS BEREND COHEN. (*Trans.*, 1914, 1892).

The paper contains a critical examination of the theory of Frankland and Wharton (*Trans.*, 1896, lxix., 1583), by which they attempt to explain the numerical relation subsisting between the rotatory power of position-isomerides when attached to an active side-chain. The author shows from the large amount of data collected by himself and his collaborators on the substituted menthyl esters of benzoic acid that the theory cannot be sustained.

203. "*Studies in Catalysis. Part I. Hydrolysis of Methyl Acetate, with a Theory of Homogeneous Catalysis.*"

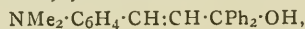
By ALFRED LAMBLE and WILLIAM CUDMORE McCULLAGH LEWIS. (*Trans.*, 1914, 2330).

Measurements of the rate of hydrolysis of methyl acetate in the presence of hydron as catalyst have been carried out at 25° and 35°, and it is shown that the temperature coefficient of the reaction is independent of the amount of the catalyst, a result which stands in opposition to the Arrhenius theory of "active" and "passive" molecules. A general theory of homogeneous catalysis is suggested, based on the magnitude of the infra-red radiation effects from hydron, and it is shown that the quantity of energy required per molecule of methyl acetate to cause it to react is of the same order of magnitude as one quantum of infra-red radiation in the region of 5 μ . Certain deductions from the theory are pointed out.

204. "The Action of Magnesium Phenyl Bromide on Derivatives of Phenyl Styryl Ketone." By IDA SMEDLEY MACLEAN and SIBYL TAITE WIDDOWS. (*Trans.*, 1914, 2169).

The product of the interaction of magnesium phenyl bromide and phenyl *p*-carbethoxystyryl ketone is *p*-carbethoxy-3,3-diphenylpropio-phenone. The corresponding acid was obtained in colourless needles melting at 184–185°; the semicarbazide melted at 220–221°.

Phenyl *p*-dimethylaminostyryl ketone, when similarly treated with magnesium phenyl bromide, gives diphenyl-*p*-dimethylaminostyrylcarbinol,—



melting at 100°.

205. "The Firing of Gases by Adiabatic Compression. Part I. Photographic Analysis of the Flame." By HAROLD BAILY DIXON, LAWRENCE BRADSHAW, and COLIN CAMPBELL. (*Trans.*, 1914, 2027).

These experiments were undertaken in order to study the initiation of the flame produced by the adiabatic compression of gases.

The gases, contained in a stout glass tube, were compressed by a piston moving between supports and forced in by a falling pendulum; the flames produced were photographed on a rapidly moving film.

The photographs showed:—

1. That the piston was not stopped at the moment the gases reached their ignition-point, but at the moment the moving force was removed.

2. That the nature of the flame depended partly on the rate at which the piston was driven in.

3. That no violent compression waves were set up, although such waves did exist when the mixtures were fired by a spark.

4. That explosive mixtures of gases did not "detonate" when they were fired by adiabatic compression, and that the real ignition-point was not synchronous with the appearance of the flame.

5. That the pre flame period is not negligible, and therefore in any determination of the ignition-temperature by this method the piston must be stopped at the beginning of the pre-flame period.

Some of the difficulties in using the method of adiabatic compression to determine the ignition-temperatures are discussed, and a number of preliminary results with mixtures of hydrogen and oxygen are given.

206. "The Firing of Gases by Adiabatic Compression. Part II. The Ignition-points of Mixtures containing Electrolytic Gas." By HAROLD BAILY DIXON and JAMES MURRAY CROFTS. (*Trans.*, 1914, 2036).

An apparatus is described by means of which gaseous mixtures may be fired by adiabatic compression according to the suggestion of Nernst (see Falk, *Journ. Am. Chem. Soc.*, 1906, xxviii., 1517; 1907, xxix., 1536). The ignition-points were calculated from the formula $\frac{T_2}{T_1} = \left(\frac{V_1}{V}\right)^{\gamma-1}$, V_1 , V_2 , and T_1 being determined experimentally. For convenience, the value of γ , the ratio

of the specific heat at constant pressure to that at constant volume, was taken as 1.4, all the gases used being diatomic. The main sources of error are discussed, and the effects of the lubricant, of changes in initial temperature and pressure of the gaseous mixture, and of the addition of other gases, are investigated.

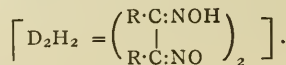
The ignition-point of electrolytic gas is found to be 526°. The addition of excess of oxygen lowers the ignition-point until the limits of inflammability are reached: this is contrary to the results of Falk, who found that the mixture $\text{H}_2 + \text{O}_2$ had the lowest ignition-point, and that the addition of more oxygen resulted in a raising of the ignition-point.

Nitrogen or hydrogen added to electrolytic gas raises the ignition-point progressively, and acts apparently as an inert gas. In the case of the former, the ignition-point may be calculated with close approximation from the formula $t^\circ\text{N} = (526 + 11x)^\circ$, where x is the number of volumes of nitrogen added to three volumes of electrolytic gas, the mixture being denoted by $2\text{H}_2 + \text{O}_2 + x\text{N}_2$. Similarly, for hydrogen mixtures, $2\text{H}_2 + \text{O}_2 + x\text{H}_2$, the ignition-point is given by the formula $t^\circ\text{H} = (526 + 18x)^\circ$. The limit of inflammability is reached roughly by the mixture containing 14 volumes of added gas to 3 of electrolytic gas.

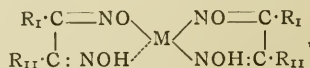
Attention is drawn to the peculiar effect of the addition of oxygen and to the fact that V_1 and T_1 remaining the same, V_2 for mixtures containing excess of hydrogen is less than the value of V_2 found for corresponding mixtures containing excess of nitrogen, and hence the calculated value for T_2 in the case of the former is greater than T_2 in the case of the latter.

207. "The Chemical Constitution of Dioximes." By LEO ALEXANDROVITSCH TSCHUGAEV. (*Trans.*, 1914, 2187).

In 1905 the author discovered a new series of complex compounds of the heavy metals corresponding with the eighth group of the periodic system, and derived from α -dioximes, for example, $\text{Ni}(\text{D}_2\text{H}_2)$, $\text{Pt}(\text{D}_2\text{H}_2)$, $[\text{Co} \cdot 2\text{NH}_3 \cdot \text{D}_2\text{H}_2]\text{Cl}$, &c.,—



The structure of these compounds, termed by the author dioximes, is discussed, and experimental evidence in favour of the general formula of the group $\text{M}(\text{D}_2\text{H}_2)$:—



is adduced.

According to this formula the dioximes are cyclic compounds, and belong to the inner complex salts.

208. "The Chlorination and Bromination of Substituted Toluenes." By JULIUS BEREND COHEN and COLIN JAMES SMITHELLS. (*Trans.*, 1914, 1907).

In former papers by Cohen and Dakin (*Trans.*, 1901, lxxix., 1111) and Cohen and Dutt (*Trans.*, 1914, cv., 501) it has been shown that the orienting effect of *o*-chlorotoluene on chlorination is very different from that of *o*-bromotoluene on bromination, and it was thought desirable to determine the influence of *o*-chlorotoluene on bromination and of *o*-bromotoluene on chlorination. At the same time the other chloro- and bromo-toluenes have been included in the present inquiry.

The results are tabulated alongside those of the two former investigations :—

Chlorination.

Bromo-toluene.	Products.	Chloro-toluene.	Products.
Ortho	2:4, 2:6	Ortho	2:4, 2:3, 2:6, (2:5)
Meta.	2:5, 3:4	Meta.	2:5, 3:4
Para.	2:4, 3:4	Para.	2:4, 3:4

Bromination.

Chloro- toluene.	Product.	Bromo- toluene.	Products.
Ortho	2 : 5, 2 : 4	Ortho	2 : 5, 2 : 4
Meta.	2 : 5, 3 : 4	Meta.	2 : 5, 3 : 4, (3 : 5)
Para.	2 : 4, 3 : 4	Para.	2 : 4, 3 : 4

It will be seen from the above table that the principal difference in the behaviour of the isomerides lies in the relative quantity and character of the products derived from the ortho-compounds, more especially if a comparison is made between the products of chlorination and bromination. The authors do not attempt to explain these irregularities.

209. *The Action of Cold Concentrated Hydrochloric Acid on Starch and Maltose.* By ARTHUR JOHN DAISH. (*Trans.*, 1914, 2053).

The hydrolysis of starch and maltose by cold fuming hydrochloric acid (D₁₅ 1.210) has been studied. In the case of starch it is probable that, as with diastatic enzymes, soluble starch, dextrin, and maltose are formed in succession, but these stages are passed through very rapidly, so that after 135 minutes 86 per cent of the theoretical quantity of dextrose has been formed. Maltose is hydrolysed to dextrose not much more rapidly than starch itself, so that although fuming hydrochloric acid decomposes starch to maltose with extreme rapidity, the production of dextrose is limited by the rate of the hydrolysis of maltose. The essential similarity of the action of acids and enzymes, especially of takadiastase, on starch is discussed. It is concluded that in both cases the dextrose which is formed as the final product is derived from maltose produced as an intermediary (Davis, *Journ. Soc. Dyers*, 1914, xxx., 249).

It is shown that, contrary to the opinion expressed by Willstätter and Zechmeister (*Ber.*, 1913, xlv., 2401), when dextrose is dissolved in ordinary concentrated or fuming hydrochloric acid, a certain amount of synthetic action always occurs, even when only 1 per cent of the sugar is present. This is made evident by a gradual rise of the specific rotatory power, and a corresponding falling off of the cupric reducing power. In the case of the fuming acid the gradual destruction of dextrose is liable to mask this effect, but in ordinary concentrated hydrochloric acid, when the destruction of dextrose takes place far more slowly, it is very apparent.

210. *The Velocity of Hydrolysis of Starch and Maltose by Cold Concentrated and Fuming Hydrochloric Acid.* By ARTHUR JOHN DAISH. (*Trans.*, 1914, 2065).

The velocity of hydrolysis of starch and maltose has been studied polarimetrically at 20.0°, and a comparison has been made with the results obtained on studying the action of enzymes on starch and maltose. It is shown in the case of maltose that the action of fuming hydrochloric acid gives a velocity-coefficient which is practically constant throughout the change, the extreme range being only about 3 per cent (0.0103 to 0.0106). The action is practically unimolecular. With soluble starch the velocity-coefficient is not constant, but rises continually during the hydrolysis (0.0052 to 0.0063), the variation being about 20 per cent. In this case the departure from the unimolecular law is due to the change taking place in successive stages.

The results obtained with ordinary concentrated hydrochloric acid and either maltose or soluble starch are similar to those obtained when enzymes act on these substances; that is to say, the velocity-coefficient calculated by a logarithmic equation is not constant, but shows considerable variation during the action. These results and the departure of the law of action of enzymes from a simple law are best explained by the view put forward by Davis (*Journ. Soc. Dyers*, 1914, xxx., 249) that in such cases a number of successive changes take place; this necessarily influences the velocity-coefficient when calculated in the ordinary way.

The action of fuming hydrochloric acid on cellulose, recently studied by Willstätter and Zechmeister (*Ber.*,

1913, xlv., 2401), is an extreme instance of an action occurring in successive stages.

211. *"The Osmotic Pressure and Physical Constitution of Caoutchouc Solutions."* By WILLIAM AUGUSTUS CASPARI. (*Trans.*, 1914, 2139).

The author has made a study of the osmotic rises exhibited against pure solvent by benzene and light petroleum solutions of caoutchouc. A convenient apparatus is described, in which the semipermeable septum consists of a cylindrical cell of porous earthenware impregnated with cold-vulcanised caoutchouc.

It is found that the osmotic rise, in the case of viscous solutions, is not proportional to the concentration, but increases much more rapidly than the same. Of solutions having the same concentration but different viscosities, the more viscous shows a higher rise than the less viscous. The conclusion is drawn that the osmotic rise is not due to pure osmotic pressure as ordinarily understood, but depends also on the physical nature of the solution, and it is sought to explain the phenomena by the hypothesis that the solutions consist of an elastic gel-phase dispersed in a sol-phase.

So far as the experiments permit of any conclusion as to the molecular weight of caoutchouc in solution, they point to a very high value, of the order of 100,000. A lower value, namely, 40,000, is indicated for gutta-percha in solution.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, November 13, 1914.

Dr. A. RUSSELL, Vice-President, in the Chair.

A PAPER on "A Bridge for the Measurement of Self-Induction" was read by Mr. D. OWEN, B.A., B.Sc.

1. An alternate-current bridge method is proposed for the determination of self-induction in terms of capacity and resistance. The inductance L is given by the relation $L = K_3 r_1 R$; in addition to which it is also necessary for balance of the bridge to satisfy the condition $K_3 r_1 = K_4 r_2$.

2. The two conditions of balance may be secured in practice without mutual interference. The end point is, therefore, rapidly attained. The possibility of effecting a balance is unlimited by the value of the unknown L .

3. The method is independent of frequency. This has the accompanying advantage that it is unnecessary to employ a pure sine voltage. Very good results may be attained with a buzzer as source and a telephone receiver as detector at, say, 500 vibrations.

4. The dependence of sensibility of the bridge on the frequency is discussed, and it is shown that over a wide range (say, 100 vibrations to 1000 vibrations) the sensibility is high.

5. The effects of residual inductance in the resistance coils and leads, and of absorption in the condensers, may be simply and correctly allowed for, the formula then becoming $L = K_3 r_1 (R - R_0)$. This fact is of especial importance in the accurate determination of very small inductances.

6. Tests are quoted showing that with the same pair of condensers measurements over the full range from one microhenry upwards may be made. For inductances of the order of 10 microhenries the error may be kept within a few parts in 1000, whilst if the inductance is as high as a few millihenries the error of any measurement may be reduced below one part in 10,000.

7. The application of this bridge to the determination of capacity in terms of self-inductance is discussed, and an example is given of a test of the temperature variation of capacity of a standard mica condenser over the range 0°–30° C.

DISCUSSION.

Mr. A. CAMPBELL congratulated the author on his clear treatment of the general case. His method had

several advantages, the most important of which was that he took a zero reading to eliminate the inductance of the leads by substituting a non-inductive resistance for the inductance to be measured. There is, of course, a difficulty in all such methods in obtaining a non-inductive resistance, but this can be got over by using a small inductance of which the value can be calculated, such as a pair of parallel wires. He could not say how far the terms in equation 12 could always be neglected, as done by the author, with frequencies greater than 1000. Particular cases could be tried to see how far this was permissible. Among the disadvantages he instanced the use of standard condensers in place of standard inductances. The latter could be obtained at less cost and of greater accuracy than condensers. Moreover, the values of condensers varied more rapidly with temperature and frequency than did those of inductances. The former defect was aggravated by the time required for a condenser to take up a steady temperature. The usual practice was to keep it at a given temperature for twenty-four hours or more in measuring to tenths or hundredths per cent. Another difficulty in bridge work with condensers is caused by earth capacities. If the point of earthing be altered different results may be obtained. He suggested that the galvanometer and battery might profitably be interchanged. The position described in the paper was the worst for disturbances due to earth capacities.

Mr. F. E. SMITH mentioned that in Rosa and Grover's paper, quoted by the author, a figure practically identical with Fig. 3 in Mr. Owen's paper appeared. Some of the equations, also, were very similar, but Rosa and Grover had, apparently, overlooked the fact that by making one of the R's and one of the L's zero the bridge could be used for the measurement of self-induction. He was surprised that Mr. Owen appeared to prefer the telephone to the vibration galvanometer in many cases. He would have expected the latter to give more satisfaction in almost all cases. With regard to the discrepancy found by the author in the temperature curve for his condenser, he might say that in the case of paraffin wax condensers it was always dangerous to cool to 0° , as a change occurred in the wax which introduced trouble. Curtis had gone into the matter of changes in the resistance of the old B.A. resistance coils when cooled to 0° , and had shown that these were due to changes in the wax.

Dr. RUSSELL said that he had used Mr. Owen's method of measuring inductance in his laboratory, and had found it simple, accurate, and most satisfactory. When ordinary alternating-current supply was available, good results were obtained either with a telephone or a vibration galvanometer. The theorem on which the method is based is extremely interesting from the theoretical point of view, and several curious results follow from it. Mr. Owen's method of proof was well adapted to the needs of electro-technical students, but he preferred the analytical methods as they were more rigorous.

The AUTHOR, in reply, referred to the variation of capacity with frequency. This was most marked at low frequencies, and as, to get sensibility, the bridge had to be used at frequencies of 100 or more, one was working outside the most dangerous region. With regard to the temperature variations, he pointed out that the condenser could always be tested against a standard inductance if need be. He had allowed four hours for his condenser to come to a given temperature. In ordinary use, as the daily range was not more than 3° or 4° C., and as 1° only introduced an error of 1 in 10,000, he thought the trouble would be inappreciable. He had tried both positions of the galvanometer and battery, and sometimes one and sometimes the other proved most satisfactory. The difficulty about earth capacities was one that had to be guarded against in all balanced bridge methods when the utmost accuracy was required. The effect was likely to be very small in the bridge described, since the capacities employed were comparatively great.

A paper "On the Coefficient of Diffusion in Dilute Solutions" was read by Mr. B. W. CLACK, B.Sc.

The paper describes modifications made in the apparatus previously described (*Proc. Phys. Soc.*, xxiv., Dec. 15, 1911) to determine the value of the coefficient of diffusion of salts through water, by means of which the steady state is hastened and results obtained more quickly.

The single wide tube previously employed is replaced by a battery of shorter and narrower tubes. The error due to end-correction is investigated, and results are given for the salts KCl, KNO_3 , and NaCl, for various concentrations down to very dilute solutions.

DISCUSSION.

Dr. GRIFFITHS said that he wished he could detect some flaw in Mr. Clack's methods, as he had always got higher results than those of the author. It appeared, however, to be much easier to get results too high than too low.

Mr. PATERSON did not see why, in a symmetrical arrangement, such as the diffusion bulbs used by the author, the syphoning on which the maintenance of the concentration at the lower end of the diffusion tube depended should take place.

Mr. F. E. SMITH wished to know if the author's method would be suitable for measuring the rate of diffusion of one solution into another of very nearly equal concentration and density. The problem was met with in standard cells. There was a slight difference in composition of the liquid throughout the cell, and this appeared to become practically constant after some years, as though diffusion had ceased altogether.

Dr. RUSSELL congratulated the author on having completed such a thorough investigation. When Glasgow University was removed to its new buildings at Gilmourhill in 1871, Lord Kelvin set up many long tubes containing liquids, with the idea that the progress of the diffusion might be noted not only after years, but after hundreds of years. Although the author's earlier experiments had lasted months in some cases, he was now able to complete them in a few days.

The AUTHOR, in reply, thought it was an accident which way syphoning started, but when started it would obviously go on. It would be difficult to apply the method to solutions of nearly equal concentration, although it would measure the diffusivity of a strong solution with respect to a weaker one of the same salt to the same degree of accuracy as it measures that of a dilute solution with respect to water, the difference of concentration being the same in each case.

MEETINGS FOR THE WEEK.

MONDAY, 30th.—Royal Society of Arts, 8. (Cantor Lecture). "The History and Practice of the Art of Printing," by R. A. Peddie.

WEDNESDAY, Dec. 2nd.—Royal Society of Arts, 8. "Britain and Germany in Relation to the Chemical Trades," by W. R. Ormandy, D.Sc.

Society of Public Analysts, 8. "Application of Spectrography to Analysis," by S. J. Lewis. "Some Oleaginous Seeds," by E. R. Bolton and Eoid M. Jesson. "Corrections in Bomb Calorimetry," by G. N. Huntley. "Determination of Sulphates in Flour," by G. D. Elsdon.

THURSDAY, 3rd.—Royal Society, "The Thermophone, a New Form of Telephone," by M. de Lange.

Chemical, 8.30. "Re-determination of the Atomic Weight of Tin," by H. V. A. Briscoe. "Isomerism of the Oximes—Part VI., β -Dimethylaminobenzaloxime," by O. L. Brady and P. P. Dunn. "Organo-derivatives of Bismuth—Part II., The Stability of Derivatives of Quinivalent Bismuth," by F. Challenger and C. F. Allpress.

Presentation.—A Gold Medal is to be presented by Mr. Henry S. Wellcome to Dr. Power, to commemorate his directorship of the Wellcome Chemical Research Laboratories for eighteen and a-half years. In addition, Mr. Wellcome is causing a life-size portrait of Dr. Power to be painted.

THE CHEMICAL NEWS.

VOL. CX., No. 2871.

THE PART PLAYED BY THE AMORPHOUS PHASE IN THE HARDENING OF STEELS.*

By J. C. W. HUMFREY, B.A., M.Sc., M.Eng.

THE existence in solid metals of an amorphous or under-cooled liquid phase has already been deduced from two distinct points of view, viz. :—

1. As being formed in the crystal gliding planes when a metal is severely overstrained. This phenomenon has been particularly studied by Beilby.

2. As normally existing as a thin film or cement between the individual crystals of which a mass of metal is built up. This theory, which was originally independently advanced by several writers, has received strong experimental support from the work of Rosenhain and Ewen, and the present author. (See References 1 to 4).

In a paper (Ref. 4) dealing with the influence of the amorphous intercrystalline cement upon the mechanical properties of metals, the author put forward a suggestion that the re-crystallisation which occurs in iron and steel at the Ar 3 change-point does not take place directly, but by the preliminary breakdown of the γ crystals to an amorphous state, followed by a subsequent formation of the β or α crystals from the amorphous. The suggestion was advanced in order to explain the continuous existence of an intercrystalline cement in iron irrespective of its allotropic changes. A somewhat similar idea was advanced many years ago by Barus and is quoted by Roberts-Austen in his *Introduction to Metallurgy* as follows :—"When iron passes through the temperature of re-calescence, its molecular condition is for an instant almost chaotic."

In the present paper the suggestion is examined further, and from it is deduced an explanation of the hardening of steels.

In the idea as originally advanced it was assumed that the amorphous cement which exists during the different allotropic ranges of iron is always of a similar nature, and corresponds in phase with that of the true liquid metal; further consideration of the matter has, however, led the author to a somewhat different view, and one, he thinks, in which the theory of the formation of an intermediate amorphous phase during re-crystallisation becomes more consistent with thermodynamical principles.

We know that a substance, in passing from the liquid to the solid (crystalline) form, changes from a state in which the units are irregularly dispersed to one in which they are arranged in some definite and regular manner, which is characteristic of the substance in question. Numerous crystallographic researches—chiefly upon crystals having a perfect external form—have resulted in a theory of crystal structure which the author believes to be now generally accepted, and which has indeed received striking confirmation from the recent experiments upon the reflection of X-rays from crystal surfaces. The theory in question asserts that the regularity of structure within a crystal is twofold, viz. :—

1. That the centres of gravity of the molecules are arranged together according to one of a series of geometrical devices called "space lattices," in which each point in the lattice is surrounded by a similar distribution of other points.

2. That in each molecule of a crystal the atoms are similarly situated.

The author considers that it is the second form of regularity which essentially gives rise to the first; or in other words, that in crystallisation from fusion it is the forces exerted by each molecule upon its neighbours (*i.e.*, forces due to the resultant reactions of its atoms) which bring about the space-lattice structure of the crystal.

Now an allotropic change must be considered as being essentially accompanied by a change in the internal structure of the molecules, *e.g.*, a reorganisation of the atoms composing them or a change in their number. Thus we have the two gaseous allotropes of oxygen, the common gas in which each molecule contains two atoms, and ozone in which each molecule contains three atoms. When an allotropic change takes place in a crystalline body we must imagine a similar internal rearrangement of the atoms in each molecule; and, if the new form which the molecules take involve a corresponding change in the external forces which they exert upon one another, then the previously existing space lattice may become unstable and a fresh one may be formed characteristic of some other crystal form. But before the reorganisation can be completed there must, at least temporarily, be a state of disorder, and it is during this disorder that the author considers that the structure must be considered as amorphous. The intermediate amorphous state may be realised as corresponding to the liquid which would be formed by the fusion of the solid phase stable at the lower temperatures, if the conditions could be so adjusted that the subsequent re-crystallisation were avoided. Certain cases are known where such a phenomenon can be actually observed. Thus in the case of sulphur the change from the monoclinic to the rhombic and *vice versa* normally occurs at a temperature of 95.6° C.; but the rhombic form stable below this temperature can be heated above it, and in this metastable condition melts at 115° C.; if, however, the change to monoclinic is allowed to complete itself before this temperature is reached, the monoclinic crystals of sulphur do not melt until 120° C.

In the case of iron the temperature-tenacity curves obtained by Rosenhain and the present author (Ref. 3) give strong indications that a similar phenomenon might occur, the rapid drop in the tenacity of both α and β iron before Ar 3 strongly suggesting that they are rapidly approaching their melting points; and that if on heating a sample of iron suitable conditions of pressure could be applied which prevented the re-crystallisation to the γ , then a true melting-point could be observed in the neighbourhood of 900° C.

We know that physical changes of state, such as from liquid to solid or from one allotropic modification to another, do not take place instantaneously throughout the whole mass of a body, but that starting from certain nuclei they proceed gradually outwards. Thus we must conceive that the intermediate amorphous phase existing during an allotropic change which occurs normally (*i.e.*, by relatively slow heating or cooling) commences to re-crystallise almost as soon as it is formed, and is present at any particular instant during the change merely as thin films or layers between the co-existing crystalline phases, the films moving forward as the change progresses. The course of the breakdown of the one crystalline phase to the amorphous would tend to follow those planes in which the freedom of movement was greatest, viz., the crystal gliding planes and possibly the intercrystalline boundaries.

That a second crystalline phase may form after the first has broken down to amorphous necessitates the condition that the mass is not too viscous for the forces of crystallisation to overcome the viscosity and to marshal the molecules into their new orientation. We know from Beilby's work that such a condition is not invariably present, since he has shown that any amorphous phase formed by severe overstrain in the cold possesses a definite stability up to certain well-marked temperatures, and only passes back into the crystalline state when these temperatures are exceeded. Thus, if an allotropic change be made, by suitable conditions, to take place at a temperature at which

* Contribution to the General Discussion on "The Hardening of Metals," held before the Faraday Society, Nov. 23, 1914.

an amorphous phase is stable, then we can conceive that while the breakdown from the one crystalline state may take place, yet the fresh crystallisation may be prevented, and that under such conditions the amorphous phase formed by the breakdown will persist. That the breakdown from a crystalline to an amorphous state may take place in spite of low temperature is clearly shown by the formation of amorphous from the crystalline by overstrain, and also by the changes in certain alloy steels to be referred to later.

In a metal in which an allotropic change normally takes place at a temperature well above that at which the viscosity is sufficient to prevent crystallisation, abnormal conditions—such as rapid cooling—may delay the change to well below this temperature.

From the general considerations which have been advanced above we may now pass to the particular case in view, viz., that of steels. Firstly we have the following experimentally determined data:—

1. Pure iron undergoes an allotropic change at about $860^{\circ}\text{C}.$, which results in a complete re-crystallisation. The latter fact has been clearly proved by "heat-reliefs" (Ref. 5), by the microscopical study of strain effects (Ref. 3), and by other experiments.

2. With increasing percentages of carbon the temperature of the change is gradually lowered until with 0.9 per cent of carbon it occurs at a minimum temperature of $680^{\circ}\text{C}.$ With less quantities of carbon than 0.9 per cent the change does not take place at one temperature, but a diminishing amount of γ iron (containing the carbon in solid solution) is retained down to $680^{\circ}\text{C}.$, where the change is finally completed.

3. A second change occurs in iron and in steels containing less than 0.45 per cent of carbon at about $780^{\circ}\text{C}.$, which change is marked by an evolution of heat on cooling, a discontinuity in the magnetic properties, and a smaller though clearly marked discontinuity in the tenacity. As to how far this change represents a truly allotropic one is a matter of some doubt, but we do know at least that it is *not* accompanied by any re-crystallisation, and for this reason does not enter into the present argument.

4. Iron at temperatures above the allotropic change-point referred to in (1) is capable of holding carbon in solid solution, but in the state which normally exists below the change-point it is incapable (or practically so) of holding it. While it seems probable that it is held in solution in the form of carbide, it is not definitely known whether it is as the carbide Fe_3C which normally forms when it is thrown out of solution at $680^{\circ}\text{C}.$; certain experiments (Ref. 6) rather tend to the contrary view.

5. The temperature at which amorphous matter formed by severe overstrain in the cold commences to re-crystallise freely on subsequent heating, and which conversely may be considered as the minimum temperature at which crystallisation can occur in an undercooled liquid mass on cooling, has been determined for mild steel by Goerens (Ref. 7) and found to be in the neighbourhood of $500^{\circ}\text{C}.$ While a certain amount of crystallisation can proceed below this temperature, it is very small when compared with that which proceeds when it is attained. It is doubtful, however, whether any very exact limits can be laid down for the maximum temperature below which the amorphous phase is stable. In the cases where it has been formed by overstrain, it is possible that the actual disturbance from the true crystalline orientation may not be the same in all places where an amorphous structure has been formed, and that therefore a lower temperature is needed to bring about sufficient freedom for the return to the crystalline structure where the disturbance has been slight than it is where the disturbance has been more severe. The fact that to each temperature to which an overstrained specimen is heated, there corresponds a certain amount of re-crystallisation (which

ceases to increase after a certain length of time at that temperature), rather lends support to such a view.

Again, it has been found impossible entirely to destroy by strain all or even the greater part of the crystalline phase, and therefore we do not know whether crystallisation in a purely amorphous mass will begin at the same temperature or with the same freedom as it would in a mass in which a considerable proportion of crystalline entities are still present; it would appear that a purely amorphous mass would be the more stable of the two.

When formed by overstrain in a normally cooled steel, the amorphous matter will be derived chiefly from the α ferrite, since the cementite is practically incapable of plastic deformation. When formed, however, by the breakdown of austenite in a carbon steel the amorphous matter will consist of a mixture of iron and iron carbide, and this mixture may not possess the same viscosity as pure iron. This consideration is referred to below from a somewhat different point of view.

Although it is evident from the above that we cannot state a very exact figure for the maximum temperature of stability of an amorphous iron-iron carbide solution, yet it is probable that, on heating, the stability must become small in the neighbourhood of $500^{\circ}\text{C}.$, and that conversely an amorphous solution undercooled below this temperature will possess a certain stability which will rapidly increase on further cooling.

From the experimental data outlined above we see, firstly, that while in the case of pure iron there is a range of about $400^{\circ}\text{C}.$ between the temperatures at which the breakdown of the γ iron occurs and that at which the re-crystallisation of α iron becomes difficult, yet in the case of 0.9 per cent carbon steel the range is reduced to less than $200^{\circ}\text{C}.$ The probability of retaining by sudden cooling some of the amorphous phase formed by the breakdown of the γ structure is therefore much greater with increasing carbon contents. But there is another factor quite apart from this lowering of the temperature of the change-point which causes the presence of carbon to still further promote the retention. Above the change-point the carbide is in solid solution in the austenite, and when this phase breaks down to amorphous the carbide molecules will still remain closely intermingled with those of the iron. Now, before the amorphous can re-crystallise, the two different kinds of molecules have to segregate, since the carbide is insoluble in either α or β iron. Such segregation must necessarily be a slow process in an undercooled viscous mass, and rapid cooling may easily allow the minimum temperature of crystallisation to be passed before it has had time to take place. A somewhat similar argument to this last has already been advanced by Rosenhain (Ref. 8), but as a reason rather for the retention of austenite than as hindering the crystallisation of α iron from amorphous.

It has been shown by Benedicks (Ref. 9) that to retain γ iron (austenite) in carbon steels pressure as well as rapid cooling is necessary; this fact also follows from the known lowering of the change-points by pressure. Now the change from a crystalline to an amorphous state in metals is, in practically all cases, accompanied by an increase in volume, and in the case under consideration this increase will be still more marked by the fact that crystalline γ iron is denser than crystalline α , and therefore much more so than amorphous α . Thus when a certain amount of γ iron has broken down to amorphous it will occupy more space in the mass and will tend to compress the γ iron that has not already changed and therefore to prevent its doing so. Quenching, therefore, besides preventing the crystallisation of the amorphous mixture formed by the breakdown of the austenite, may at the same time preserve a certain amount of that austenite unchanged. The more severe the quenching, the more austenite retained, since the rapid increase in rigidity of the amorphous mass as it cools will enable it to exert its pressure more effectively

The theory of hardening of steels outlined above depends upon two points: (1) that the temperature of the change-point is lowered by quenching, and (2) that during a normal allotropic change there must exist a temporary amorphous state. The influence of the first point has already been advanced by Grenet (Ref. 10), the second now shows how this lowering of the change-point may bring about hardness, since it involves the retention of the amorphous state, and such a state is known to be one of particular hardness in practically all metals.

We may now pass to the consideration of how the theory agrees with, and is consistent with, the known physical properties and microstructure of carbon steels hardened by quenching, and of certain alloy steels which possess a similar hard structure even when slowly cooled.

Physical Properties.—The physical properties of a steel hardened by quenching and the same material hardened by overstrain are in many ways similar, and strongly point to the idea that a similar form of structure is present. Thus in both cases it has been found that the hard metal possesses a distinctly lower specific gravity than the same samples when annealed. Among other properties in which overstrained and quenched steels vary in a similar manner from the annealed metal may be cited the possession of high retentivity, coercive force, and co-efficient of hysteresis. The fact pointed out above, that in overstrained steel the carbide and the iron molecules will remain segregated, while in a quenched steel they will be very intimately mixed in solution, may prevent the similarity from being too close.

Microstructure.—The typical micro-constituent of a quenched steel is martensite, which may—according to the carbon contents and the rate of quenching—vary from an almost structureless mass to a strongly marked duplex structure of interlacing needles, the latter type being characteristic of high carbon contents and rapid cooling. According to the present theory the duplex structure consists of the two constituents γ iron (austenite) and an amorphous solution of α iron and carbide; the form in which the two constituents occur together being due, as advanced above, to the tendency of the austenite crystals to break up most readily along their gliding planes. Conditions which produce an almost structureless martensite are those under which, while practically all austenite has been able to change to amorphous, yet little or no re-crystallisation of the amorphous has been possible. Such conditions occur in practice when samples are quenched from not too high a temperature; in such a state a steel should possess its maximum hardness combined with a freedom from internal stresses, and therefore be in the most favourable condition from a practical point of view. Rapid quenching from too high temperatures, which results in the retention of much of the austenite, will produce a less satisfactory result, since besides the fact that austenite is known to be less hard than the amorphous solution, its presence implies internal stresses and liability to hardening cracks and spontaneous fractures. These points are of course well known to all who have dealt with the hardening of steels.

Alloy Steels.—The present theory of hardening applies with special aptness to the case of certain alloy steels, which acquire a hard structure even when slowly cooled. Alloy steels, of which the nickel-carbon series may be taken as typical examples, are found when normally cooled to possess three different types of structure according to the percentage of these elements which they contain, viz. (a) pearlitic, (b) martensitic, or (c) austenitic. The increasing percentages of the added elements produce a progressive lowering of the change-point, and it has been found that the structure of type (a) occurs in all steels in which the critical point lies above about $400^{\circ}\text{C}.$; of type (b) in all the steels in which the change-point lies between about $400^{\circ}\text{C}.$ and atmospheric temperature; and of type (c) in all the steels in which the change-point lies below atmospheric temperature. The last type, however, become martensitic if undercooled to below their change-point.

These results show that in all the steels in which a change-point occurs below $400^{\circ}\text{C}.$ —a temperature which corresponds very approximately to that below which we have seen the amorphous phase is stable—possess a structure and a hardness which is similar to that of a quenched carbon steel. The present theory exactly accounts for such a phenomenon, since it states that when the breakdown from the γ condition takes place at a temperature at which the amorphous phase is stable, a hard amorphous structure will persist. The fact that the partial change to amorphous can, and does, occur in these steels in spite of low temperature is evidence that the breakdown of a crystalline condition is possible in spite of low temperature.

Two further points may be emphasised in regard to the bearing of the present theory upon the normal austenitic or martensitic structure of alloy steels.

1. Cold work applied to an austenitic alloy causes a new and intensely hard constituent to appear along the slip planes of the γ crystals (Ref. 11, 12), and this constituent has been shown to possess all the characteristics of martensite. The quantity produced by a given amount of deformation is out of all proportion to the amount of amorphous phase formed by an equal amount of deformation in other metals. If we consider, as the present theory suggests, that the crystals in an austenitic steel are in most cases within less than $100^{\circ}\text{C}.$ of a temperature at which they spontaneously change to an amorphous state, it is conceivable that when once a certain breakdown occurs along a slip plane due to the deformation, it may proceed with much greater freedom than it would in the case of an ordinary metal in which no such spontaneous change is involved.

2. The present theory offers an explanation of the irreversible nature of the changes which occur in alloy steel, i.e., that the change from the austenitic to the martensitic structure takes place at a much lower temperature than the reverse change on heating. It suggests that while the change from the γ state to the amorphous on cooling is independent of low temperature, yet the completion of the change, which would be the re-crystallisation of the amorphous to α , is prevented by it, and that in consequence the amorphous phase persists. The reverse change of amorphous to γ crystals on heating will be prevented by precisely the same cause, viz., that crystallisation of any kind cannot take place until the viscosity has sufficiently diminished to allow of the necessary molecular movements. It has been found that about $400^{\circ}\text{C}.$ is the minimum temperature at which the change on heating occurs in any of the series of irreversible alloys, and this temperature may therefore be assumed to be the maximum at which an amorphous solution of iron, nickel, and carbide is stable. It will be remembered that it is the same as the temperature at which the change occurs in the alloys which first show a martensitic structure on normal cooling.

Reference may be made at this point to the "high speed" steels. The re-crystallisation either on heating or cooling of an amorphous solution will depend particularly upon its viscosity, and the viscosity itself upon the temperature and the composition of the mixture. In high-speed steels we have the two properties, firstly that of air hardening, and secondly that of the stability of the hard structure to high temperatures. The latter property appears to be given to the steels by elements such as chromium, tungsten, &c., which are known to form definite carbides. It appears probable that these carbides act by greatly increasing the viscosity of an amorphous solution containing them, and so allow the amorphous state to remain stable at much higher temperatures.

Tempering.—The tempering of hardened steels will, according to the present theory, consist in the progressive crystallisation of the amorphous solution formed by the quenching, but the process is possibly rather more complicated than would at first sight appear to be the case, since, from the experiments of Campbell and Haskins, previously referred to, it appears to be accompanied by

polymorphic changes in the composition of the carbide. The first segregation of an undercooled solution of a iron and iron carbide would, however, agree very well with Benedick's theory of troostite as a colloidal system. It seems possible that the segregation of the two different kinds of molecules might advance some way before an actual crystalline structure, however fine, is formed; in such a condition the structure would correspond to that of a true liquid colloidal solution. We can in this way distinguish between the two constituents troostite and sorbite, the former being a partially segregated amorphous mixture of iron and iron carbide, while the latter is an extremely fine crystalline mixture of the same constituents.

It may be noted that the temperature at which a steel loses all the hardness which it has acquired by quenching agrees very approximately with that at which it loses any hardness acquired by overstrain.

Summary.—The conclusions arrived at in the present paper may be summarised as follows:—

The hard structure which can be produced in carbon steels by quenching and in certain alloy steels by normal cooling, is due to the presence of a hard amorphous solution of a iron and iron carbide, which solution may be compared to Beilby's amorphous phase formed by overstrain.

To explain the formation of this amorphous phase the author advances a theory that the passage of a substance from one allotropic modification to another of different crystalline form involves the temporary formation of an amorphous state, corresponding to the liquid phase of the modification about to be formed. In steels such a change occurs at Ar₃; and if, due to sudden cooling or to the presence of certain alloyed elements, the change-point is lowered to a temperature below that at which crystallisation in the viscous mass becomes difficult, then the amorphous form will be retained in a metastable form in the cold.

References.

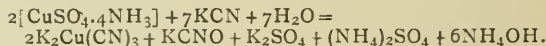
1. Rosenhain and Ewen—"Intercrystalline Cohesion in Metals," *Journ. of the Inst. of Metals*, No. 2, 1912, vol. viii.
2. Rosenhain and Ewen—"Intercrystalline Cohesion of Metals," second paper, *Journ. of the Inst. of Metals*, No. 2, 1913, vol. x.
3. Rosenhain and Humfrey—"The Tenacity, Deformation, and Fracture of Soft Steel at High Temperatures," *Journ. of the Iron and Steel Inst.*, 1903, No. 1.
4. Humfrey—"The Influence of Intercrystalline Cohesion upon the Mechanical Properties of Metals," *Iron and Steel Inst.*, *Carnegie Memoirs*, 1913.
5. Humfrey—"The Intercrystalline Fracture of Iron and Steel," *Iron and Steel Inst.*, *Carnegie Memoirs*, 1913.
6. Campbell and Haskins—"Effects of Heat Treatment on the Colorimetric Test for Carbon in 0.32 per cent Carbon Steel," *Journ. of the Iron and Steel Inst.*, 1913, No. 2.
7. Goerens—"On the Influence of Cold Working on the Properties of Iron and Steel," *Iron and Steel Inst.*, *Carnegie Memoirs*, 1911.
8. Rosenhain—"Recent Advances in the Metallography of Steel," *Staffordshire Iron and Steel Inst.*, 1910.
9. Benedicks—"The Cooling Power of Quenching Velocities, &c.," *Journ. of the Iron and Steel Inst.*, 1908, No. 2.
10. Grenet—"The Transformations of Steel within the Limits of the Temperatures Employed in Heat Treatment," *Journ. of the Iron and Steel Inst.*, 1911, No. 2.
11. Carpenter, Hadfield, and Longmuir—"On the Properties of a Series of Iron-Nickel-Manganese-Carbon Alloys," Seventh Report of the Alloys Research Committee, Institute of Mechanical Engineers, Nov. 17, 1905.
12. Rosenhain—"Deformation and Fracture of Iron and Steel," *Journ. of the Iron and Steel Inst.*, 1906, No. 2.

DETECTION OF CYANIDES IN THE PRESENCE OF FERRO- AND FERRICYANIDES AND THIOCYANATES.

By O. L. BARNEBEY.

THE reaction upon which this detection is based is the solubility of copper sulphide in solutions of alkali cyanides. When hydrogen sulphide is passed into a dilute ammoniacal cupric solution a precipitate of cupric sulphide is formed, or a deep blue to brownish black coloration is imparted to the solution, depending upon the amount of hydrogen sulphide dissolved, the temperature, and the dilution of the solution. The addition of an alkaline cyanide clears this suspension or coloured solution. The copper solution can be made so dilute that the test becomes quite delicate, much more delicate than the bleaching of the blue solution of copper ammonia compounds, and has the additional merit of not being interfered with seriously by ferro- or ferricyanides, or thiocyanates.

An ammoniacal copper solution was prepared by dissolving 1.25 grms. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in water, making ammoniacal, and diluting to a litre. Each cc. of this solution is equivalent to about 0.000473 gm. of hydrocyanic acid on the basis of the following reaction, which, however, is empirical:—



The test is performed as follows:—A bubble or two of hydrogen sulphide gas is passed into, or a few drops of hydrogen sulphide water are added to a small quantity of the standard copper solution, the amount of this depending upon the delicacy desired. This suspension is then added to the unknown ammoniacal solution (or *vice versa*) with constant shaking. If the colour is bleached, the presence of a cyanide is indicated. The addition of the ammoniacal copper solution is continued until no further bleaching is noticed. From the volume of copper solution used an approximate quantitative estimation can be made. With care, one can add a few cc. of dilute hydrogen sulphide water in the cyanide titration of copper at the instant of bleaching, and obtain a coloration which is then bleached with more cyanide, making a moderately accurate end-point. In the presence of ferrocyanides, however, the reaction is not quantitative, inasmuch as the ferrocyanide is oxidised to ferricyanide more or less completely during titration.

The colour caused by 0.1 cc. of the copper solution in a volume of 5 cc. is bleached by 0.2 cc. of a 0.01 N solution of KCN when the test is made as above indicated, which means a delicacy of about 1.0 part HCN per hundred thousand.

In the presence of 50 cc. of a solution of KCNS (equivalent to 2 grms.) 0.5 mgrm. of HCN can be detected; 50 cc. of a 4 per cent solution of $\text{K}_3\text{Fe}(\text{CN})_6$ (2 grms.) allows a detection of 1 mgrm. of HCN; while 50 cc. of a 4 per cent solution of $\text{K}_4\text{Fe}(\text{CN})_6$, (*i.e.*, 2 grms.) will likewise permit a detection of 0.5 mgrm. of HCN. In the presence of small quantities of the above cyanogen compounds the test is reliable to 0.1 mgrm. of HCN.

In the presence of smaller amounts of ferro- or ferricyanides the test becomes correspondingly more delicate. When the test is applied to solutions containing much ferricyanide, one should add as much copper solution to a blank, containing approximately the same amount of ferricyanide, as to the solution being tested for cyanide, and the difference in shade should be noted, or the quantities of copper solution necessary to give a certain depth of colour should be compared.

For the average requirements of qualitative analysis, tenth-normal copper sulphate solution will suffice.

Inasmuch as the test gives a decided reaction for relatively small amounts of cyanides, and also furnishes an indication of the relative amount present in the solution

examined, as well as being applicable in presence of other cyanides, this test is proposed for general qualitative purposes.—*Journal of the American Chemical Society*, xxxvi., No. 6.

THE FREEZING-POINT OF MILK.*

By J. BROWNLIE HENDERSON, F.I.C., and L. A. MESTON.
(Continued from p. 261).

A. A. BONNERNA (*Zeit. f. Nahrungs- und Genussmittel*, 1908, xv., 34) points out an inaccuracy in Winter's formula for calculating the percentage of added water.

Suppose a milk to contain W per cent of water, then the crystalloids which cause the depression of the freezing-point in 100 grms. of milk are dissolved in W grms. of water. If X grms. of water are now added to 100 grms. of milk, the crystalloids are dissolved in (W+X) grms. of water.

Now let D be the observed freezing-point of the diluted milk expressed in —° C. then—

$$X = \frac{0.55 \times W}{D} - W.$$

As the value W can easily be calculated when the percentages of fat and the specific gravity are known, the value of X can also be obtained.

This formula, however, is not accurate from a theoretical point of view, because on diluting with water the electrolytic and hydrolytic dissociation of the salts is increased, and consequently the freezing-point decreased. This error is, however, sufficiently compensated for practical purposes if the calculation is based on the volume instead of the weight. The error thus introduced compensates the one arising from the increased dissociation.

Examples of Bonner's Formula.

Milk.

Specific gravity	1.0142
Total solids (weighed)	5.9
Freezing-point	—0.255

$$X = \frac{0.55 \times 94.1}{0.255} - 94.1 = \frac{(203 \times 94.1) \times 100}{203} =$$

53.64 per cent water by weight.

53.64 × 1.0142 = 54.4 per cent water by volume against 53.7 per cent water by volume calculated by Winter's formula.

Milk.

Specific gravity	1.0298
Total solids	11.97
Freezing-point	0.526

$$X = \frac{0.55 \times 88.03}{0.526} - 88.03 = \frac{(92.04 - 88.03) \times 100}{92.04} =$$

4.35 water by weight.

= 4.48 water by volume against 4.32 water by volume according to Winter's formula.

Summary of Table III.

Results from legal samples of milk obtained during the last three years:—

In fifty-four samples out of sixty-three the water shown by the freezing-point is from 0.2 to 9.9 per cent higher than that shown when calculated on 8.5 per cent solids not fat, the average being 4 per cent. In five cases, the calculation of added water on 8.5 per cent solids not fat and the freezing-point are practically identical.

In the other three cases the added water on 8.5 per cent solids not fat is from 1.7 to 3.9 per cent lower than by the

freezing point. In the 3.9 per cent case the acidity was not determined.

TABLE III.—Showing Results from Legal Samples of Milk obtained during the last Three Years, containing under 8.5 per Cent of Solids not Fat.

Total solids.	Fat.	Solids not fat.	Nitrogen.	Ash.	Freezing-point.	Acidity.	Added H ₂ O calculated on 8.5 s.n.f. Per cent.	Added H ₂ O calculated on f.p. Per cent.
Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	°C.			
11.8	3.5	8.3	0.40	0.70	—0.520		2.6	5.4
11.5	3.2	8.3	0.50	0.68	—0.485	14.4	3.0	11.8
11.1	2.8	8.3	0.45	0.66	—0.480		3.0	12.7
11.6	3.3	8.3	0.49	0.69	—0.490		3.1	10.9
12.5	4.3	8.2	0.43	0.68	—0.495	13.6	3.4	10.0
11.6	3.4	8.2	0.48	0.70	—0.530		3.5	3.6
10.7	2.5	8.2	0.41	0.68	—0.528		3.8	3.9
11.5	3.3	8.2	0.49	0.66	—0.530	14.0	4.0	3.6
11.3	3.2	8.1	0.47	0.70	—0.524		4.5	4.7
11.5	3.4	8.1	0.47	0.66	—0.480		4.6	12.7
11.2	3.1	8.1	0.48	0.68	—0.510		4.7	7.2
11.9	3.8	8.1	0.44	0.68	—0.520	14.0	4.7	5.4
12.0	3.9	8.1	0.47	0.70	—0.505	12.0	4.7	8.1
11.4	3.3	8.1	0.48	0.68	—0.517		4.7	5.9
11.1	3.0	8.1	0.46	0.71	—0.510		5.0	7.2
11.6	3.5	8.1	0.47	0.72	—0.520		5.0	5.4
11.1	3.0	8.1	0.46	0.71	—0.510		5.0	7.2
11.4	3.4	8.0	0.47	0.69	—0.497	13.2	5.9	9.6
11.8	3.8	8.0	0.44	0.67	—0.505	12.0	5.9	8.1
11.0	3.0	8.0	0.49	0.72	—0.525	12.0	5.9	4.5
11.1	3.1	8.0	0.44	0.69	—0.515	12.0	5.9	6.3
10.9	2.9	8.0	0.48	0.63	—0.475		5.9	13.6
10.5	2.6	7.9	0.41	0.70	—0.460		6.6	16.5
11.0	3.1	7.9	0.45	0.64	—0.490		7.1	10.9
11.2	3.3	7.9	0.45	0.65	—0.470		7.1	14.5
11.0	3.2	7.9	0.46	0.62	—0.475		7.9	13.6
11.5	3.7	7.9	0.44	0.67	—0.500	12.8	7.6	9.1
11.8	3.9	7.9	0.44	0.67	—0.495		7.3	10.0
11.0	3.2	7.8	0.45	0.68	—0.472		8.2	14.1
11.3	3.5	7.8	0.47	0.63	—0.458	12.4	8.2	16.8
11.6	3.8	7.8	0.46	0.64	—0.507		8.2	7.7
10.9	3.1	7.8	0.48	0.64	—0.496	12.0	8.2	9.8
11.3	3.6	7.7	0.44	0.62	—0.505	12.8	8.8	8.1
11.5	3.8	7.7	0.44	0.61	—0.452	12.4	10.1	17.7
11.2	3.5	7.7	0.46	0.63	—0.470		9.4	14.5
11.3	3.6	7.7	0.46	0.65	—0.477	14.0	9.4	13.2
10.6	2.9	7.7	0.45	0.67	—0.494		9.4	10.1
11.2	3.5	7.7	0.46	0.66	—0.484		9.4	11.9
10.8	3.1	7.7	0.45	0.63	—0.492		9.4	10.5
11.8	4.1	7.7	0.47	0.65	—0.470		9.4	14.5
11.2	3.6	7.6	0.44	0.60	—0.475	13.2	10.1	13.6
10.2	2.6	7.6	0.41	0.65	—0.465	13.0	10.1	15.5
11.6	4.0	7.6	0.49	0.64	—0.502	12.0	10.4	8.7
10.6	3.0	7.6	0.43	0.64	—0.502		10.6	8.7
10.8	3.3	7.5	0.46	0.65	—0.467		11.8	15.1
10.9	3.4	7.5	0.44	0.62	—0.448		12.2	18.4
10.2	2.8	7.4	0.41	0.63	—0.500		13.0	9.1
10.2	2.9	7.3	0.42	0.61	—0.477		14.1	18.2
10.1	2.8	7.3	0.41	0.60	—0.455	12.8	14.1	17.3
9.7	2.4	7.3		0.62	—0.455		14.1	17.3
10.1	2.9	7.2	0.42	0.60	—0.451		15.3	17.9
10.0	2.8	7.2	0.41	0.58	—0.433	12.0	15.3	21.2
9.4	2.3	7.1	0.48	0.58	—0.425		16.1	22.7
10.1	3.0	7.1	0.41	0.64	—0.440		16.1	20.0
10.0	3.0	7.0	0.41	0.56	—0.433		17.7	21.2
10.0	3.0	7.0	0.38	0.54	—0.425		17.7	22.7
10.4	3.5	6.9	0.44	0.61	—0.430	9.2	18.2	21.8
9.6	2.8	6.8	0.39	0.57	—0.425		20.5	22.7
8.9	2.2	6.7	0.38	0.56	—0.420	14.0	21.2	23.6
9.8	3.6	6.2	0.41	0.54	—0.407	8.0	26.8	25.9
7.7	1.9	5.8	0.36	0.48	—0.377	9.2	31.8	31.4
5.9	1.9	4.0	0.25	0.37	—0.255		52.4	53.6
5.3	1.5	3.8	0.23	0.33	—0.220		55.3	60.0

(To be continued).

* From the *Proceedings of the Royal Society, Queensland*, xxiv., 165.

RADIUM.*

(Continued from p. 266).

Resources.

RADIUM ores are known to occur in several localities, but always in comparatively small amounts. The richest radium-bearing region is undoubtedly the Paradox Valley region in Montrose County, Colo., where the ore is carnotite, containing uranium and vanadium besides radium. Mines at Joachimsthal, Austria, have been taken over by the Austrian Government and are being developed through governmental resources. The only ore there is pitchblende, an impure oxide of uranium carrying radium. Pitchblende is also found in Gilpin County, Colo., whence several tons of ore have been shipped abroad to contribute a little to the radium supply.

In the old tin-mining district in Cornwall, England, some pitchblende is also found, and an English company and one of the French companies are reputed to get their chief supplies from low-grade ores on the dumps and in the slopes of the old tin mines.

Deposits of autunite, another radium-bearing mineral, are known to occur in Portugal and also in Australia, and a few hundred mgrms. of radium are yearly produced from these ores. Carnotite is, however, the chief source of radium at present. Very low-grade deposits of carnotite mixed with another mineral (ilmenite) are known to occur in Australia, and a plant has been started in that country which is producing from 100 to 200 mgrms. of radium per month. A deposit has also been found at Ferghana, Russian Turkestan. It has not yet become a regular source of supply, and there is no reason to believe, from any report issued up to the present time, that it will prove a large source of radium. In fact, no deposit of radium ores anywhere discovered gives any promise of supplying material enough to meet the immediate demands.

The carnotite deposits of Colorado and Utah are, as before stated, the most extensive in the world. They have, however, been very wastefully exploited, some four tons more or less of low-grade ore having been thrown on the dumps or mixed with mine waste for every ton of shipable ore so far marketed.

Present Ore Supplies.

According to the testimony presented to your committee, from 700 to 1000 claims have been at one time or another staked in Colorado and Utah; of these claims perhaps 300 may eventually be worked and 150 may be considered reasonably good. These claims have been for the main part bought up by a few interests, and for only a few claims as the prospector obtained more than 50 dols. to 200 dols. a claim. The Standard Chemical Co., of Pittsburgh, controls approximately 170 of these claims; the General Vanadium Co., of Liverpool, England, 58; the Radium Co. of America, 20 to 25; Thomas F. Curran, 70 or more; O. B. Wilmarth, 20 to 25; and the National Radium Institute, 16. The others are scattered among the smaller producers. Many claims are being located at present, and if a supply of radium is to be preserved for America prompt action by Congress is necessary.

Future Ore Supplies.

As to future ore supplies no definite statements can be made, the testimony presented to your committee being contradictory. Those who now own claims are very sure that other supplies will be found in quantity. There is no reason to believe that further discoveries will not be made, although the mining engineers reporting to the Denver Chamber of Commerce, the employees of the Bureau of Mines, and members of the Geological Survey, state that all known deposits are already located. Accordingly, it will probably be necessary, if the Government is to secure

immediate supplies, to purchase from owners of claims already located as well as to put forth every effort to open up new deposits.

The carnotite region is known to be extensive, there being an area of something over 480,000 acres within which pockets of carnotite are apt to occur. But in many places the carnotite-bearing stratum has been eroded away and in many others it is so deeply buried by later beds that there is no reasonable hope of ever obtaining the supplies that are undoubtedly embedded therein. There are, however, certain areas where this stratum is only a few feet under the surface, as well as many places on the canyon sides where it outcrops and where pockets of carnotite are likely to be found. These carnotite deposits, however, are mainly small, no claim having yet produced without exhaustion more than 500 tons of shipable ore. Most of the pockets contain less than 50 tons. These pockets are not connected by stringers and there is no evidence of vein formation. Accordingly, the finding of one pocket is no indication that others are adjacent, although sometimes this may be the case. With the large number of prospectors now in the field it is hoped and expected that new discoveries will be made and that sufficient bodies of ore will be opened up to assure the radium necessary for American hospitals.

Saving of Waste.

Many of the claims already worked have on their dumps considerable quantities of ore that is too poor to ship at such prices as have prevailed in the past. There is every reason to believe, however, that concentration methods can be developed by which much of this ore can be concentrated on a basis that will make a large part of it available for use.

This is a very important work for the Government to do, as more than twice as much radium has been wasted than has actually found its way to market. Certainly every effort should be made to conserve this almost priceless material.

A paper presented to the American Mining Congress at Philadelphia October 24, 1913, reprinted as Appendix 1 of this report, gives additional data.

United States Production and Exportation.

This country has been quite unaware of the proportion of uranium ores sent abroad. As in most radium ores there is a fairly definite ratio of radium to uranium (1 to 3,000,000), the amount of radium obtained and exported can be roughly calculated from the uranium content of the ores sold. According to the figures of the Bureau of Mines, carnotite ores carrying 28.8 tons of uranium oxide were produced in 1912, and practically the entire amount was exported. In that year the uranium content of the major part ran between 2 and 3 per cent uranium oxide, as, owing to the cost of transportation, no ore carrying less than 2 per cent could be marketed. From the ores shipped abroad in 1912, 11,443 grms. of anhydrous radium bromide could have been and probably was extracted. In 1913, according to preliminary figures of the United States Geological Survey, 2140 tons of ore were produced, of which 1198 tons were shipped to works in this country and 942 tons were exported. However, owing to the cost of transportation only the richer ores were exported, so that radium equivalent to about 7.5 grms. of anhydrous radium bromide, more than one-half of the total American production for the year, was sent abroad. One foreign company did not work its plant in the Paradox Valley, Colo., during the greater part of the year, because it was building a new plant in Liverpool, and it cost less to leave the ore in the mine than to take out the ore and store it in England. This company will be a large exporter of carnotite from Colorado and Utah during 1914.

It is improbable that all of the ores exported are now represented by finished product, but the actual production for 1912 and 1913 cannot be much less than the quantity mentioned. The total quantity of uranium exported in

* Report No. 214, presented to the House of Representatives, U.S.A., at the 63rd Congress.

1911 was almost equal to that exported in 1912, and ores are still being sold for treatment abroad. There can be no doubt that in 1912 and 1913 there was obtained from America ores more than twice and probably three times as much radium as from all other sources combined.

The carnotite prospects and mines of the West have been described in Bulletin 70 of the Bureau of Mines, entitled "A Preliminary Report on Uranium, Radium, and Vanadium," by R. B. Moore and Karl L. Kithil; and the subject is further treated in "Advance Chapters from Mineral Resources for 1912," by F. L. Hess, of the United States Geological Survey. The mines are for the main part in Montrose and San Miguel Counties, Colo., and in a somewhat more extensive territory just to the west and north-west of these deposits in Utah. Since Bulletin 70 was written prospecting in this region has been extensive. Many agents of foreign manufacturers have been in the country seeking supplies for shipment abroad, and a much stronger demand for ores has caused prices to advance, so that at present ore containing 2 per cent of uranium oxide readily brings 80 dols. per ton at the railroad at Placerville, Col. Correspondingly higher prices are obtained abroad, and some private producers who were able to contract for considerable quantities report even higher prices.

Owing to the interest aroused and to the proposed withdrawal of radium-bearing lands, there has been a decided increase in prospecting and some important new finds have been made. Although many claims have been staked in different parts of the radium-bearing region, the most important finds have been at the summit of Big Canyon at the head of Lisbon Valley, Utah, just across the State line from the McIntyre district, Colorado. Other important finds are reported in the Henry Mountains, about 100 miles south east of Green River and in a district about 7 miles north-east of Monticello, Utah. Development work has been carried on at Gateway and also in the western part of the Paradox Valley, the original scene of the main operations.

Foreign Demand.

As already stated, by far the larger part of the radium ore so far produced in the United States has been shipped abroad, and, even worse than this, that portion of the radium which is being extracted in America has also been largely contracted for foreign delivery. This has opened up to foreign medicine and science opportunities for the investigation and treatment of malignant diseases that have been denied to our own people, except by purchase of manufactured radium compounds at almost prohibitive prices. To-day there is probably less than 2 grms. of radium salts in the possession of physicians in this country, which, considering the almost miraculous cures of cancer shown to this committee by reputable surgeons through the means of plaster casts and photographs, is appalling. In Europe a very different condition exists. During the past year extensive appropriations have been made there for the purchase of radium and mesothorium, showing the great demand that has arisen for these materials in the treatment of cancer. Some of these purchases have been made by Government appropriation and some by municipal or other public subscription. The Austrian Government has expended 600,000 dols. for the purchase of deposits of radium-bearing ores, and has made subsequent provision for the mining of these ores and the extraction of the radium. Prussia has appropriated 370,000 marks for the purchase of 1 gm. of radium bromide.

Radium in Cancer Work.

Three leading surgeons of this country, who have themselves had extensive experience in the application of radium in the treatment of malignant diseases, viz., Dr. Howard A. Kelly, of Baltimore; Dr. Robert Abbe, of New York; and Dr. Curtis F. Burnham, of Baltimore, have appeared before this committee and have shown casts and photographs of cancer cures actually brought

about in their practice, which appear to your committee to be in themselves more than sufficient argument for the proposed legislation. These three surgeons and Dr. H. R. Gaylord, director of the New York State cancer laboratory, have favoured the general principles outlined in this bill, have expressed their inability to procure more radium for their own practice, and have emphasised their great need and desire for more of this material to be used in treating the sufferers of the most malignant of diseases.

We appropriate large sums each year for the treatment of the diseases of animals, for the destruction of pests, and various sums for other important objects for the benefit of the people. It has been demonstrated beyond a doubt that this remedy is a cure for external malignant growths.

Hoffman, the statistician, estimates that each year 75,000 people die from these growths known as malignant.

If this remedy will cure 20 per cent we have saved 15,000 lives each year. The cause of cancer is to-day unknown, so physicians must apply themselves to the cure until some one discovers the cause, so that it will be known how to prevent this disease.

If this Government does not secure these ores bearing radium, it is quite likely that large quantities will be shipped out of the country, and what is extracted in our own country will fall into the hands of those who will have a monopoly, and the price will be so high that it will be out of the reach of the poor people. As it has been well said, "cancer is the poor man's disease and radium is the rich man's remedy."

If this bill becomes a law we hope that in time the Government will control this remedy so that it may be placed in all parts of the country, readily accessible to all those who may be so unfortunate as to require its use and may secure the treatment without having to pay an exorbitant price. We want it so placed that the poor as well as the rich may be cured.

It certainly is better for the Government to have the monopoly than the private individual, in so important a curative agent for disease from which no one can be assured they will never be afflicted.

It is now estimated that the hospitals belonging to the United States ought to have at least 25 grms., and at the present price it would cost 120,000 dols. per gm., which would mean the expenditure of a large sum to secure the amount thought necessary. It has been shown that foreign buyers have been securing all the ore they could and shipping it to their own country and extracting the metal, and then our people have been compelled to buy the radium from them. It seems too important that this very valuable curative agent should be allowed to go from our own country to foreign lands and we not be able to secure sufficient for the use of our own people. While we would not desire to be selfish and not permit those of other countries who might need this remedy to secure it, yet we should also remember that our first duty lies to our citizens, and we should have the opportunity of securing a sufficient supply first before we sell to any other country. We should, of course, assist those who may be unfortunate in any place in the world, that they may have the benefit so far as we are able to do, yet we ought to have the control of this remedy, which lies in the public lands which the Government now owns.

Radium Institutes.

Several radium institutes have been founded throughout the world for studying the application of radium to science and to disease. Some of these are private and some are public. Prominent among them may be mentioned the Radium Institute of Austria, founded under a donation given by Dr. Kuppelweiser to the Academy of Science of Austria, which now has one of the largest supplies of pure radium salts used chiefly in scientific investigations.

In Paris a new radium institute under the direction of the Sorbonne has been built by this university near the Pantheon.

In England the London Radium Institute was founded by Sir Ernest Cassel and Viscount Iveagh, who gave a large sum for its endowment. This institute is making a special study of the application of radium to disease.

In this country the National Radium Institute has recently been founded by Dr. Howard A. Kelly, of Baltimore, and Dr. James Douglas, of New York. The reasons for the foundation of this institute and its purposes may be best expressed by quoting the article by the secretary of the institute, Mr. Archibald Douglas, which appeared in the Mining and Scientific Press of January 3, 1914, and is reprinted at Appendix 2 of this Report.

Difficulty of Securing Radium on any other Basis than Government Operation.

At present, on account of the tremendous demand for the material abroad, there is no means of keeping radium ores or radium in America except by overbidding the excessive price now being offered for them in European markets; and this means that the people of this country must buy back from foreign countries at speculative and exorbitant prices the very radium which was their own and which their Government has allowed to become subject to foreign exploitation. It has already been shown that foreign Governments and municipalities are prepared to pay prices for radium far in excess of the cost of production and manufacture, and they have already obtained more than half of the available ores produced in the United States. It was in France, Germany, and Austria that the value of radium was first appreciated. Here a demand for it was first established and processes for extracting it from these ores were developed. Meanwhile, our own Government has been giving away its deposits of radium-bearing ores, which even though limited are the most extensive known, and allowing them to pass into the ownership of a foreign corporation, a few American companies acting as shipping agents for other foreign corporations, or to an American company which sells its radium largely to foreign purchasers. The high price of radium salts—by far the larger part of this price representing a profit to the manufacturer—is taking radium out of the country, and even if it stays in the country, the present price makes its use so expensive that the material can hardly be expected to be available to people of small means, except in so-called charity cases.

Accordingly, it seems extremely important that the United States Government shall make such provision as may be necessary to obtain supplies of radium requisite to meet the more urgent needs of the American people.

For this neglect and delay in radium development in the United States the responsibility does not rest with the 75,000 cancer sufferers, but rather with the scientific men in our universities and our Government service and with Congress itself. The legislation now proposed is intended to remedy this situation.

Appropriations.

The committee after due deliberation has asked for an appropriation of 150,000 dols. for the erection and general equipment of a suitable building or buildings for radium-extraction and other work of the Bureau of Mines in the metal-mining States, and the further sum of 300,000 dols. for the necessary expenses connected with the purchase and treatment of radium-bearing ores and the extraction of radium therefrom during the fiscal year ending June 30, 1915. The committee believes that these amounts are less than should be allotted to this important work, but believes also that they will be sufficient for the erection and equipment of the extraction plant and the purchase of such ores as can be procured in the fiscal year 1915, and will enable the department to get the work well under way.

It is expected that the buildings to be erected under this appropriation of 150,000 dols. will be inexpensive structures that will be located at points best adapted to the success of this radium work. The larger part of this appropriation is for the engineering equipment necessary in

the concentration and treatment of the ores and the extraction of the radium. The other appropriation (300,000 dols.) will be used for the purchase of ores (covering the cost of mining) and for the chemical equipment and supplies and general operating expenses.

It is expected further that if the necessary supply of ore be obtained the commercial value of the radium extracted under this appropriation will be far in excess of the total amount of the appropriation authorised in this bill.

Your committee believes that the welfare of the American people, and especially the alleviation of those suffering from that terrible malignant disease known as cancer, demand that this bill be passed and that this important work be initiated without undue delay.

Further information concerning the radium resources of the United States and the progress made in their development, including the establishment of the National Radium Institute, will be found in the two appendices reprinted below.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

(Continued from p. 269).

212. "*Studies in Phototropy and Thermotropy. Part V. Polymorphic 4-Hydroxybenzylidenearylamines produced by Trituration and by the Influence of Sunlight.*" By ALFRED SENIER and ROBERT BENJAMIN FORSTER. (*Trans.*, 1914, 2462).

Various 4-hydroxybenzylidenearylamines were prepared and examined in the hope of discovering further instances of phototropic and thermotropic phenomena amongst the members of a class of compounds in which trituration-dimorphism had already been detected (Senier and Shephard, *Trans.*, 1909, xcv., 1951, 1954).

It is incidentally found that dimorphism effected by trituration is a general character of 4-hydroxybenzylidenearylamines, and, further, that their behaviour in this respect is parallel to that of mercuric iodide, which below 126° changes by trituration from its yellow to its red dimorphic variety.

Most of the compounds examined are thermotropic, and some exhibit phototropy, and in most cases a third polymorphic form is produced by the prolonged action of actinic light.

213. "*The Condensation of Furan-2:5-Dialdehyde with Malonic Ester and Malonic Acid.*" By WILLIAM FRANCIS COOPER and WALTER HAROLD NUTTALL. (*Trans.*, 1914, 2218).

Furan-2:5-dialdehyde condenses with two molecules of ethyl malonate, forming *ethyl furan-2:5-dimethylenemalonate*, which, on hydrolysis, gives the corresponding *acid*. This acid forms two peculiar isomeric additive compounds with acetic acid. On crystallising the yellow tetracarboxylic acid from glacial acetic acid, a brown pentabasic acid results, which is a compound of one molecule of the original tetracarboxylic acid with one molecule of acetic acid. The other additive pentabasic compound of the two acids, isomeric with the above but red in colour, is obtained when furan-2:5-dialdehyde is condensed with malonic acid, using glacial acetic acid as catalyst.

The only difference between the isomerides is apparently one of colour, which is not affected by repeated recrystallisation from glacial acetic acid.

On esterification, all three acids, namely, the yellow tetracarboxylic, and the brown and red pentabasic acids, give the same *ethyl furan-2:5-dimethylenemalonate*, which is identical with that obtained by the direct condensation of furan-2:5-dialdehyde with ethyl malonate.

On condensing furan-2:5-dialdehyde with malonic acid in the presence of pyridine, a brown, amorphous product results, which is probably a mixture of stereoisomerides of *juvan* 2:5-diacyrylic acid. It gives a crystalline ester on esterification with ethyl alcohol, whilst, on reduction with sodium amalgam, *juvan*-2:5-dipropionic acid is formed. If the reduction is carried out with aluminium filings, an intermediate acid, containing two atoms of hydrogen less than the dipropionic acid, results.

214. "Catalysis. Part XVIII. The Reactions of both the Ions and the Molecules of Acids, Bases, and Salts; the Reactions of Alkyl Haloids with Phenoxides and Ethoxides." By JOHN HANSTON SHRODER and SOLOMON FARLEY ACREE.

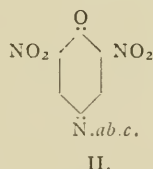
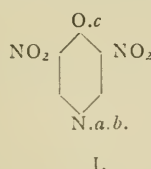
The older work of Hecht, Conrad, and Brückner and the recent investigations by Segaller show that the velocities of the reactions of alkyl haloids with phenoxides and ethoxides can be expressed by the purely empirical equation, (1) $K'_N = K_N + a \log (V'/V)$. All this work can, however, be interpreted in terms of Acree's theory that both the ethoxide (phenoxide) ions and the non-ionised ethoxide (phenoxide) react with the alkyl haloids according to the equations (2) $K_N = K_i + K_n(1-a)$, (3) $K'_N = K_i + K_m(1-a')$, &c. The empirical equation (1) holds, therefore, because the experimental data give approximate constants for "a" in the equation (4), $a = a' - a/\log(V'/V)$, derived from a comparison of equations (1), (2), and (3), and (1) becomes practically identical with (2) and (3).

215. "Synthetical Experiments in the Group of the iso-Quinoline Alkaloids. Part IV. The Synthesis of β -Gnoscopine." By EDWARD HOPE and ROBERT ROBISON. (Trans., 1914, 2085).

A detailed description of work of which a preliminary account has already appeared (Proc., 1912, xxviii., 16).

216. "Quinone-ammonium Derivatives. Part IV. Products of the Extreme Alkylation of Alkylated isoPicramic Acid." By RAPHAEL MELDOLA and WILLIAM FRANCIS HOLLELY. (Trans., 1914, 2073).

The alkylation of mono- and di-methylisopicramic acid and of mono- and di-benzylisopicramic acid by methyl and ethyl sulphate under various conditions has led to the conclusion that in most cases the two isomeric compounds I. and II. are formed simultaneously. Of these I. represents a phenolic ether (anisidine or phenetidine derivative), and II. a true quinone-ammonium compound. A member of the latter series containing an asymmetric nitrogen atom in which *a*, *b*, and *c* stand respectively for methyl, ethyl, and benzyl has been prepared.



217. "Organo-derivatives of Bismuth. Part I. The Preparation and Properties of some Tertiary Aromatic Bismuthines and their Halogen Derivatives." By FREDERICK CHALLENGER. (Trans., 1914, 2210).

The interaction of triphenylbismuthine dibromide and magnesium phenyl bromide in ethereal solution does not give tetraphenylbismuthonium bromide, but derivatives of tervalent bismuth seem to be exclusively produced, triphenylbismuthine, diphenylbromobismuthine, and phenyldibromobismuthine being isolated from the reaction mixture.

When treated with magnesium ethyl bromide, triphenylbismuthine dibromide gives triphenylbismuthine, diphenylbromobismuthine, and bromobenzene.

The instability of the bismuthonium haloids is also shared to a less extent by the bismuthine dibromides; for

example, triphenylbismuthine dibromide loses bromo benzene on boiling its solution in benzene, diphenyl bromobismuthine being obtained.

When diphenylbromobismuthine reacts with magnesium *a* naphthyl bromide, *diphenyl-a-naphthylbismuthine* is produced. This melts at 119°, and forms a yellow crystalline dibromide, melting at 140°.

Tri-*a*-naphthylbismuthine (Proc., 1913, xxix., 76) also forms a yellow dibromide melting at 120°.

On attempting to prepare diphenylethylbismuthine by the interaction of diphenylbromobismuthine and magnesium ethyl bromide an unexpected result was obtained, triphenylbismuthine and triethylbismuthine being produced.

Phenyldibromobismuthine, which forms yellow needles melting at 206°, is obtained by the action of bromine on diphenylbromobismuthine, both in chloroform solution. Bromobenzene is split off, and if excess of bromine is employed some bismuth bromide is obtained.

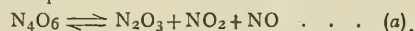
218. "*p* Toluoylactic Acid, *o*-Nitro-*p*-toluoylactic Acid, and 6:6'-Dimethylindigotin." By JAMES COOPER DUFF. (Trans., 1914, 2182).

Founded on the work of Needham and Perkin on *o*-nitrobenzoylactic acid (Trans., 1904, lxxv., 148), which acid has since been found to give indigotin when reduced with dilute sodium hydroxide solution and zinc dust, the preparation of the corresponding nitro-*p*-toluoylactic acid has been undertaken. *o*-Nitro-*p*-toluoyl chloride is condensed with ethyl acetoacetate, whereby ethyl *o*-nitro-*p*-toluoylacetate is obtained in colourless plates. On hydrolysis the ester yields *o*-nitro-*p*-toluoylactic acid, which when dissolved in dilute sodium hydroxide solution and warmed gives 6:6'-dimethylindigotin.

The preparation of ethyl *p*-toluoylacetate and *p*-toluoyl-acetic acid from *p*-toluoyl chloride and ethyl acetoacetate is also described.

219. "The Dissociation of Gaseous Nitrogen Trioxide." By BERNARD MOUTAT JONES. (Trans., 1914, 2310).

The vapour density of dry nitrogen trioxide has been determined at a series of temperatures, pressures, and volumes, varying from 15° to 139°, and 106 mm. to 818 mm. The densities obtained vary from 35.07 to 24.00 (*H*=1). The numbers obtained agree fairly closely with the assumption that the "dry" nitrogen trioxide dissociated according to the equation—



this dissociation being nearly complete at 140°, and the nitrogen trioxide not dissociating further. At the same time owing to incomplete drying there are present some "wet" NO_2 (and N_2O_4) and NO molecules which do not unite to give nitrogen trioxide or take part in equation (a), which is only concerned with "dry" molecules.

The dissociation constant for equation (a) at different temperatures has been calculated,—

$$K = \frac{\text{CN}_4\text{O}}{\text{CN}_2\text{O}_3\text{CNO}_2\text{CNO}} \cdot V^2,$$

and the values obtained indicate that at temperatures in the neighbourhood of the boiling-point (+3°) the trioxide consists mainly of N_4O_6 , and the blue colour of the very dry liquid as compared with the green colour of ordinary "wet" specimens is accounted for.

220. "The Volumetric Determination of Carbon in Aliphatic Substances in the Wet Way." By EGERTON CHARLES GREY. (Trans., 1914, 2204).

A method is described for the determination of total carbon, which is based on the oxidation of the substance by potassium dichromate, and phosphoric acid to carbon dioxide or a mixture of carbon monoxide and acetic acid. The carbon dioxide is measured, and the acetic acid is distilled from the residual fluid and titrated with $\text{N}/30$ -baryta. The method gives accurate results.

When the substance is oxidised quantitatively to carbon dioxide only 2 or 3 centigrams. need be used, but about a decigram. is required when acetic acid has to be determined.

The acetic acid is formed from the substances containing the methyl group in the chain, and the method therefore gives simultaneously some indication of the constitution of the substance.

With a modification of the apparatus described, the method would be well adapted to microchemical analysis.

Ethyl alcohol is oxidised practically quantitatively to acetic acid, and may be accurately determined in dilute solutions by this method.

The analyses of several typical aliphatic substances are given.

221. "*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part VII. Some Normal Esters of the Carbinols of the Formula $C_2H_5 \cdot CH(OH) \cdot R$.*" By JOSEPH KENYON. (*Trans.*, 1914, 2226).

The fourteen members of the "ethyl" series of carbinols of the general formula $C_2H_5 \cdot CH(OH) \cdot R$, which were described in Part IV., have been converted into the corresponding acetates and *n*-heptates. Whereas the carbinols exhibited special exaltations in rotatory power at the positions where the growing chain contained five and six and also ten and eleven carbon atoms, it is found that the rotatory powers of the corresponding acetates show this special exaltation to only a very slight extent.

In addition, fourteen normal esters from the acetate to the stearate) of *d*- γ -nonanol have been prepared, and their rotatory values determined at temperatures up to 200° for light of three different wave-lengths. As the series is ascended it is found that there are special exaltations in molecular rotatory power at the positions where the number of carbon atoms in the growing acyl group is five and ten and eleven respectively.

When the molecular rotatory powers of these esters are determined in 5 per cent ethyl-alcoholic solution it is found that these special exaltations are non-existent, whilst when the determinations are made in carbon disulphide solution the exaltations give place to depressions.

222. "*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part VIII. The Optical Rotatory Powers of the Normal Esters of Methylbenzylcarbinol.*" By JOSEPH KENYON and ROBERT HOWSON PICKARD. (*Trans.*, 1914, 2262).

Fourteen normal esters (from the acetate to the stearate) of *d*-methylbenzylcarbinol have been prepared, and their rotatory powers determined at temperatures up to 200° for four different wave-lengths. As the series is ascended, the molecular rotatory powers increase, the regularity of the increment being interrupted by a special exaltation exhibited by the *n* valerate. The "temperature-rotation" coefficients decrease on ascending the series, but the curves for the acetate and propionate exhibit a region of "anomalous" rotatory dispersion at and above 140°, whilst in 5 per cent solutions in carbon disulphide the rotatory powers of all the esters have a different sign from those exhibited in the homogeneous state.

All observations of the rotatory power of *d*-methylbenzylcarbinol and these fourteen esters can be correlated on one "characteristic diagram."

223. "*Experiments on the Conversion of certain Dibromides of the Type of Ethylene Dibromide into the Corresponding Glycols.*" By ERNEST GRAHAM BAINBRIDGE. (*Trans.*, 1914, 2291).

The author has found that glycol diacetate can be hydrolysed by boiling with a dilute alcoholic solution of sodium ethoxide, a yield of 85 per cent of the theoretical being readily obtainable. Investigations were also carried out with dilute alcoholic solutions of sodium hydroxide and sodium acetate. Hydrolysis was effected by means of these agents, but the yields were smaller than in the case of sodium ethoxide.

This method of hydrolysis proved successful with the diacetates of trimethyleneglycol and α -butylene glycol. Propylene glycol diacetate and ψ -butylene glycol diacetate cannot be hydrolysed by this means.

The author has also investigated the action of certain metallic acetates on dibromides, and finds that propylene bromide, isobutylene bromide, and ψ -butylene bromide are partly converted into α -bromo- Δ^a -propylene, α -bromo-3-methyl- Δ^a -propylene, and 3-bromo- ψ -butylene respectively.

224. "*The Metallography of German Silver.*" By FRANK CHARLES THOMPSON. (*Trans.*, 1914, 2312).

As a result of the employment of the "principle of maximum work" and of high-power microscopic examination, there is reason to believe that the oxygen present in commercial German silver is present as exceedingly finely divided zinc oxide.

Deoxidants, for example, manganese and aluminium, exert marked influence in refining the structure of these alloys, when annealed after cold working.

As the amount of nickel in the German silver is increased, the size of the crystals for the same treatment by heat becomes much finer, and at the same time the tendency for the "as cast" structure to persist despite thermal and mechanical treatment is increased.

By overheating German silver a new dendritic structure is developed, and crystal twinning may be almost entirely removed.

In alloys containing an appreciable percentage of lead or tin respectively, free lead and a material which is probably a copper-tin compound are found.

225. "*Electromotive Forces in Alcohol. Part IV. Combinations of the Hydrogen and Calomel Electrodes.*" By REGINALD FURNESS, ROBERT TAYLOR HARDMAN, and EDGAR NEWBURY. (*Trans.*, 1914, 2302).

The electromotive forces of various combinations of the hydrogen electrode with the calomel electrode have been determined, anhydrous alcohol being used throughout. The effects of the addition of sodium and lithium chlorides to the cell-liquid of the hydrogen electrode in alcoholic hydrogen chloride, and also that of the addition of small quantities of hydrogen chloride to the cell-liquid of the calomel electrode in alcoholic sodium and lithium chlorides, have also been made. Finally, electromotive forces of combinations containing saturated alcoholic solutions of sodium chloride in both compartments have been determined.

From an analysis of the numbers obtained it may be concluded that the hydrogen electrode gives nearly correct results in alcoholic hydrogen chloride, as is also the case with the calomel electrode in dilute alcoholic sodium chloride. In the presence of alcoholic hydrogen chloride, however, all measurements with the calomel electrode are untrustworthy.

The potential attained by the hydrogen electrode in N/500 alcoholic hydrogen chloride appears to be about 6 millivolts below the theoretical value.

226. "*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XX. Isomeric Solvents.*" By THOMAS STEWART PATTERSON and ERNEST FERGUSON POLLOCK. (*Trans.*, 1914, 2322).

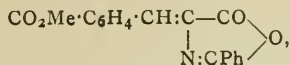
The rotations of isobutyl malate and of ethyl tartrate have been examined in a number of different solvents, and the results are discussed in connection with the various types of isomerism.

227. "*Some Derivatives of Ortho-vanillin.*" By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON. (*Trans.*, 1914, 2376).

The authors have prepared the benzoic acid, benzyl alcohol, cinnamic acid, phenylpropionic acid, hydrindone, and other simple derivatives of the *o*-veratric series. The condensation of *o*-veratraldehyde with ethyl cyanoacetate leads to the production of 8-methoxycoumarin-3-carboxylic acid, and by the nitration of the aldehyde, 6-nitro-*o*-veratraldehyde is produced which furnishes 4:5:4':5'-tetramethoxyindigotin.

228. "*Some Derivatives of isocoumarin and iso-Carbostyryl.*" By DAVID BAIN, WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON. (*Trans.*, 1914, 2392).

By the condensation of methyl phthalaldehyde with hippuric acid, 2-phenyl-4-o-carboxymethylbenzylidene-oxazolone,—



is formed, and on hydrolysis this yields isocarbostryl carboxylic acid.

By an analogous method the authors have prepared 7:8-dimethoxyisocarbostryl, from which isooxyberberine is derived.

ω-Opianoylacetophenone, prepared from silver opianate and *ω*-bromoacetophenone, when treated with alkaline condensing agents, yields 3-benzoyl-7:8-dimethoxyisocoumarin, but when potassium opianate is condensed with *ω*-bromoacetophenone, *ω*-benzoylbromomethylmeconine is formed, which, on treatment with alkalis, also yields 3-benzoyl-7:8-dimethoxyisocoumarin.

229. "Diketo-5:6-dimethoxyhydrindene." By WILLIAM HENRY PERKIN, jun., WALTER MORRELL ROBERTS, and ROBERT ROBINSON. (*Trans.*, 1914, 2405).

The method previously described for producing 1:2-diketohydrindene (*Trans.*, 1912, ci., 232) by the hydrolysis of isonitroso-1:2-diketohydrindene with formaldehyde and hydrochloric acid has now been applied to the preparation of 1:2-diketo-5:6-dimethoxyhydrindene and 1:2-diketo-5:6-methylenedioxyhydrindene.

230. "Overvoltage." By EDGAR NEWBERRY. (*Trans.*, 1914, 2419).

It has been shown that during the electrolysis of an acid solution with metal electrodes the gas before liberation penetrates the metal surface, and on emerging breaks open the surface. If a colloid is present, some of it is carried into the metal along with the gas.

The presence of a colloid in all cases raises the hydrogen overvoltage of a metal, and diminishes the degree of ionisation of the gas liberated. The overvoltage during deposition of a metal is affected to a much smaller degree.

The overvoltage of the metal and the ionisation of the gas liberated show an inverse relationship.

The overvoltage of a metal is determined by three factors, namely, (1) supersaturation of the electrodes with gas in the molecular condition, the accumulation of this gas being brought about through the permeability of the metal to ions, and the inability of the free gas to escape except by solution or breaking the metal surface; (2) deficiency or excess of non-hydrated ions in the immediate neighbourhood of the electrodes; and (3) inductive action of the escaping ionised gas on the electrodes.

Under certain conditions the third factor is sufficiently powerful to reduce the measured overvoltage of a metal to a negative quantity.

231. "Adiabatic and Isothermal Compressibilities of Liquids between one and two Atmospheres' Pressure." By DANIEL TYRER. (*Trans.*, 1914, 2534).

The method of determining the adiabatic compressibility of a liquid, described in a previous paper (*Trans.*, 1913, ciii., 1675) has been modified and improved. Extended measurements have been made for various liquids over fairly wide ranges of temperature. Results for eighteen liquids have now been completed. From the results values of the ordinary isothermal compressibility β have been calculated by aid of the following thermodynamical equation:—

$$\beta = \alpha + \frac{T \left(\frac{dy}{dt} \right)^2}{JvC_p}$$

where α is the adiabatic compressibility, v the specific volume, J the mechanical equivalent of heat, and C_p the specific heat at constant pressure.

In addition, for each liquid, accurate determinations of the specific volume at different temperatures have been made, and from the results values of dv/dt have been calculated for use in the above equation. It has been

found that the results of many earlier investigators, among whom may be mentioned Quincke (*Ann. Phys. Chem.*, 1883, [iii.], xix., 401) and Grassi (*Ann. Chim. Phys.*, 1851, [iii.], xxxi., 437), are really adiabatic and not isothermal, as supposed by their authors and as entered in various physico-chemical tables. They agree well with the present determinations of the adiabatic compressibility, and are altogether discordant with the isothermal results.

232. "The Colouring Matters of *Rhamnus catharticus*." By JOSEF OESCH and ARTHUR GEORGE PERKIN. (*Trans.*, 1914, 2280).

According to Tschirch and Polacco (*Arch. Pharm.*, 1900, ccxxviii., 459), the berries of *R. catharticus* contain (as glucoside) the yellow colouring matters rhamnocitrin, $\text{C}_{13}\text{H}_{10}\text{O}_5$, rhamnolutin, $\text{C}_{15}\text{H}_{10}\text{O}_6$, rhamnochrysin, $\text{C}_{13}\text{H}_{10}\text{O}_7$, and β -rhamnocitrin, $\text{C}_{13}\text{H}_{10}\text{O}_5$, in all of which methoxy-groups are absent. Krasowski (*Journ. Russ. Phys. Chem. Soc.*, 1908, xl., 1510), on the other hand, could isolate only rhamnetin and quercetin, and considered that rhamnolutin is possibly rhamnetin, whereas rhamnocitrin is exactly like quercetin and rhamnetin. Again, instead of rhamnochrysin, a mixture of quercetin and emodin was obtained. The results of the present investigation show that rhamnocitrin, $\text{C}_{16}\text{H}_{12}\text{O}_6$, is a monomethyl ether of kæmpferol; that rhamnolutin, $\text{C}_{15}\text{H}_{10}\text{O}_6$, the main colouring matter, is kæmpferol, whereas β -rhamnocitrin present in small amount is rhamnetin, $\text{C}_{16}\text{H}_{12}\text{O}_7$. Incidentally, it was found that pure acetyl-rhamnetin melts at 190–192°. As indicated by Krasowski, quercetin can also be obtained from these berries, but the amount detected was trifling. The presence of a substance corresponding with rhamnochrysin could not be confirmed.

(To be continued).

NOTICES OF BOOKS.

Chemical Technology and Analysis of Oils, Fats, and Waxes. By Dr. J. LEWKOWITSCH, M.A., F.I.C. Fifth Edition. Volume II. London: Macmillan and Co., Ltd. 1914.

THE second volume of the fifth edition of this comprehensive work deals with the commercial preparation of the raw materials used in the oil, fat, and wax industries, and the technology of the natural products is exhaustively discussed. Methods of preparing, refining, and examining them are described, and the processes commonly used in the detection of adulterants are thoroughly explained. The volume has been edited by Mr. G. H. Warburton, who was for many years associated with the late Dr. Lewkowitsch in his analytical practice; a large amount of hitherto unpublished information has been added to it, and the statistical and numerical data have been brought down to date.

An Introduction to Geology. By C. J. GARDINER, M.A., M.A., F.G.S. London: G. Bell and Sons, Ltd. 1914.

THIS book is not intended to be used as a text-book, but as a general introduction to the study of geology for those who are interested in the subject but have very little previous knowledge of it. It begins with short biographical accounts of some of the founders of modern geology, Werner, Hutton, William Smith, and Sir Charles Lyell, and their achievements and the advances due to them are shortly described. Then the agencies which are at work modifying the crust of the earth are discussed, and the effects of denudation, deposition, and land elevation are explained. The characters of the sedimentary rocks and the nature and distribution of their fossils are next taken up, and chapters on the connection between geology and scenery, the formation of coal, the effects of volcanoes, &c., form some of the most interesting parts of the book, which concludes with some hints upon fossil and rock collecting.

A Text-book of Physiological Chemistry. By OLOF HAMMARSTEN. Authorised translation by JOHN A. MANDEL, Sc.D. Seventh Edition. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1914.

THIS edition of Prof. Hammarsten's valuable work has been prepared from the eighth German edition, in which many important changes were made. Much new matter was added to the text, including descriptions of fresh methods and theoretical explanations, and the whole was very carefully revised in collaboration with Prof. S. G. Hedin, of the University of Upsala. The translation follows very closely the German text, and will be very welcome to English-speaking biochemists.

British Industry and the War. By J. TAYLOR PEDDIE. Institute of Industry and Commerce.

THE proposed Institute of Commerce and Industry deserves the whole-hearted support of British manufacturers, who should not fail to get a copy of this pamphlet explaining its aims and proposed constitution. In the introductory articles the lessons which the nation can learn from Germany are emphasised, and the urgent need for improvements in our commercial educational system is explained; the editor also gives a very clear account of the basis of national economics. In addition a full report is given of the speeches made at the inaugural luncheon, when Lord Grey gave an Address dealing with his Dominion House scheme. Other speakers included Sir Charles Macara and Sir George Reid, who made a very forceful and stirring speech upon the new project, which will undoubtedly benefit the whole trading community of this country.

The London Matriculation Directory. No. 68, September, 1914. London: University Tutorial Press, Ltd.

THERE are no new features in this guide, which contains as heretofore the papers set in the last examination, with solutions and criticisms, and also the report for 1914 of the Principal of the University Correspondence College. The book contains much information relating to the College's courses for matriculation and other examinations, and is an almost indispensable possession for intending candidates, who will derive much help from it, whether they intend to become students of the College or not.

The Magnet of Commerce. Published by the Great Central Railway Co.

THIS book has been issued by the Great Central Railway Company to provide the coal-owner and colliery manager, and also manufacturers and exporters, with reliable information about the coal resources of the United Kingdom, and especially about the Midland coalfield, the developments of which are considered in detail. Statistics are given relating to coal consumption, and a very full description is included of the new docks which have been constructed at Immingham to deal with the coal traffic. These new docks have the very great advantage of being accessible at all states of the tide, and elaborate arrangements have been made to deal expeditiously with the huge volume of traffic passing through them.

Pharmaceutical Society of Great Britain.—The first evening meeting of the present session will be held in the Society's Lecture Theatre on Tuesday, December 8, 1914, when a discussion will take place on "The Effect of the War on the Nation's Supply of Drugs and Chemicals," and the following are expected to deal with the subject from specific points of view within the range of their own expert knowledge:—Prof. H. G. Greenish, F.I.C., R. R. Bennett, B.Sc., F.I.C., F. W. Gamble, C. A. Hill, B.Sc., F.I.C., and J. C. Umney, F.C.S. The chair will be taken at 8 p.m. precisely.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clix., No. 12, September 21, No. 16, October 19, No. 17, October 27, 1914.

These numbers contain no chemical matter.

No. 18, November 3, 1914.

Dioxytriazines.—J. Bougault.—Good yields of dioxytriazines can be obtained by the action of a dilute aqueous solution of soda upon the semi-carbazones of α -ketonic acids in the cold. The operation is very slow, sometimes even lasting for months. The oxidation of the dioxytriazines by sodium hypobromite breaks the chain in such a way as to leave the nitrogen attached to the carboxyl of the α -ketonic acid; thus from benzyldioxytriazine phenyl propionic amide, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CONH_2$, is obtained after reduction with zinc and acetic acid.

MISCELLANEOUS.

Alchemical Society.—The next General Meeting, to be held at 1, Piccadilly Place, W., on Friday, December 11, at 8.15 p.m., will be in the nature of a Symposium, to which Messrs. Arthur Edward Waite, Gaston De Mengel, D. N. Dunlop, Lt.-Col. Jasper Gibson, V.D., LL.B., and others will contribute.

"The Electrician" Electrical Trades' Directory and Handbook for 1915.—The Thirty-third Edition of this Directory and Handbook, now in preparation, will be ready in January, 1915. It contains very carefully compiled lists of British, Colonial, and Foreign Electrical Engineers, Electric Light and Power and Electric Railway and Tramway Engineers and Contractors, Electricians, Consulting and Manufacturing Electro-Chemists and Metallurgists, Plant, Machinery, and Apparatus Manufacturers, Electrical, Telegraph, and Scientific Instrument Makers, Electricity Supply, Electric Railway and Tramway, Telegraph, and Telephone Companies, Telegraph and Telephone Engineers and Contractors, Electric Cable and Wire Manufacturers, and of all persons engaged in Electrical Pursuits throughout the world; useful Technical and Commercial Tables and Engineering Data relating to Electric Light and Traction, Electric Power Transmission, British and Colonial and Foreign Electricity Supply, and Electric Traction Undertakings (Municipal and Company), Industrial Applications of Electricity, Telegraphs and Telephones, Wireless Telegraphy, British and Foreign Government Departments, &c.; and an interesting Biographical Section, giving particulars of the careers of about 250 eminent men connected with Electricity in all its applications.

MEETINGS FOR THE WEEK.

MONDAY, 7th.—Royal Society of Arts, 8. (Cantor Lecture). "The History and Practice of the Art of Printing," by R. A. Peddie.

— Royal Institution, 5. General Meeting.

TUESDAY, 8th.—Biochemical Society, 5.30. (At the Lister Institute, Chelsea Gardens, S.W.). "Determination of Molecular Weights," by G. Barger. "Estimation of Glucose in Blood," by H. Maclean. "Van Slyke's Method of Estimating Amino-nitrogen," by O. Rosenheim. "Pregl's Method of Analysis of Carbon, Hydrogen, and Nitrogen" and "Kjeldahl's Method of Estimating Nitrogen (Bang)," by C. Funk and J. C. Drummond. "Analysis of Aliphatic Compounds by Moist Combustion," by E. C. Grey. Demonstrations of "Micro Methods" of Analysis.

WEDNESDAY, 9th.—Royal Society of Arts, 8. "Domestic Metal Work of the Eighteenth Century," by W. A. Young.

THURSDAY, 10th.—Royal Society. "The Electrical Conductivity of Echinoderm Eggs, and its Bearing on the Problems of Fertilisation and Artificial Parthenogenesis," by J. Gray. "The Endemic Flora of Ceylon, with reference to Geographical Distribution and Evolution in General," by J. C. Willis.

FRIDAY, 11th.—Alchemical, 8.15.

THE CHEMICAL NEWS.

VOL. CX., No. 2872.

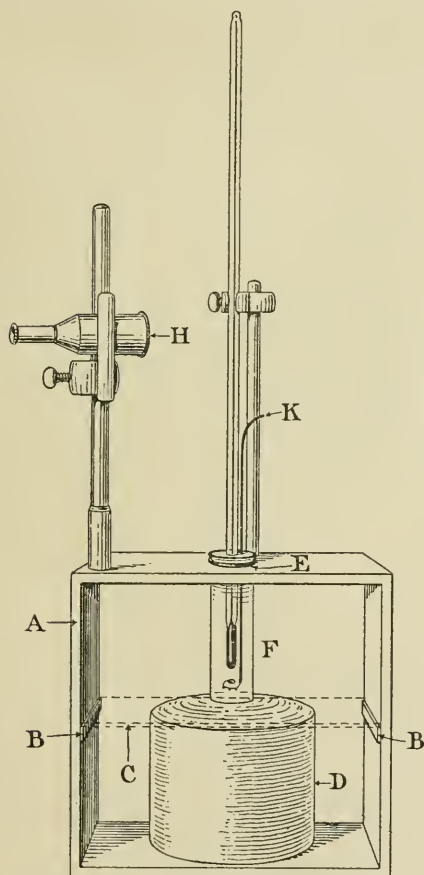
THE FREEZING-POINT OF MILK.*

By J. BROWNLIE HENDERSON, F.I.C., and L. A. MESTON.

(Concluded from p. 275).

THE following is a description of the method and apparatus that have been used in the Government Chemical Laboratory, Brisbane, for the last three years. The diagrammatic sketch shows the arrangement of the very simple apparatus required.

A is a stand made of wood 1 cm. thick, 30 cm. high, 31 cm. wide, and 18 cm. deep. Two rests, B, at a height of 9 cm. carry a movable shelf, C, on which the vessel con-



taining the freezing mixture stands. We use a porcelain beaker, D, 16 cm. high by 10 cm. wide, for a freezing vessel, and tie around it, for insulation, a roll of flannel to the thickness of about 1 inch.

A circular hole, E, centrally situated in the top of the stand, carries the milk tube, F. We use a flat-bottomed tube, 14 cm. deep and 3 cm. diameter, for holding the milk sample. We find it much easier to get agreeing results with this size of tube than with the longer round-bottomed tube recommended by Winter.

TABLE IV.—Giving the Number of cc. of Added Water per Litre of Milk Examined, corresponding to the Temperatures $-0^{\circ}550'$ to $-0^{\circ}351'$ C. ("Les Nouveaute's Chimiques pour 1905," p. 276, par Winter).

Temperature observed. Degrees below zero.	Cc. of added water in 1 litre of sample.	Temperature observed. Degrees below zero.	Cc. of added water in 1 litre of sample.
0'550	0'0	0'450	181'8
0'549	1'8	0'449	183'6
0'548	3'6	0'448	185'4
0'547	5'4	0'447	187'3
0'546	7'3	0'446	189'1
0'545	9'1	0'445	190'9
0'544	10'9	0'444	192'7
0'543	12'7	0'443	194'5
0'542	14'5	0'442	196'4
0'541	16'3	0'441	198'2
0'540	18'2	0'440	200'0
0'539	20'0	0'439	201'8
0'538	21'8	0'438	203'6
0'537	23'6	0'437	205'4
0'536	25'4	0'436	207'3
0'535	27'2	0'435	209'1
0'534	29'1	0'434	210'9
0'533	30'9	0'433	212'7
0'532	32'7	0'432	214'5
0'531	34'5	0'431	216'4
0'530	36'4	0'430	218'2
0'529	38'2	0'429	220'0
0'528	40'0	0'428	221'8
0'527	41'8	0'427	223'6
0'526	43'6	0'426	225'4
0'525	45'4	0'425	227'3
0'524	47'3	0'424	229'1
0'523	49'1	0'423	230'9
0'522	50'9	0'422	232'7
0'521	52'7	0'421	234'5
0'520	54'5	0'420	236'4
0'519	56'3	0'419	238'2
0'518	58'2	0'418	240'0
0'517	60'0	0'417	241'8
0'516	61'8	0'416	243'6
0'515	63'6	0'415	245'4
0'514	65'4	0'414	247'3
0'513	67'3	0'413	249'1
0'512	69'1	0'412	250'9
0'511	70'9	0'411	252'7
0'510	72'7	0'410	254'5
0'509	74'5	0'409	256'4
0'508	76'4	0'408	258'2
0'507	78'2	0'407	260'0
0'506	80'0	0'406	261'8
0'505	81'8	0'405	263'6
0'504	83'6	0'404	265'4
0'503	85'4	0'403	267'3
0'502	87'3	0'402	269'1
0'501	89'1	0'401	270'9
0'500	90'9	0'400	272'7
0'499	92'7	0'399	274'5
0'498	94'5	0'398	276'4
0'497	96'4	0'397	278'2
0'496	98'2	0'396	280'0
0'495	100'0	0'395	281'8
0'494	101'8	0'394	283'6
0'493	103'6	0'393	285'4
0'492	105'4	0'392	287'3
0'491	107'2	0'391	289'1
0'490	109'1	0'390	290'9
0'489	110'9	0'389	292'7
0'488	112'7	0'388	294'5
0'487	114'5	0'387	296'4
0'486	116'4	0'386	298'2
0'485	118'2	0'385	300'0
0'484	120'0	0'384	301'8
0'483	121'8	0'383	303'6

* From the *Proceedings of the Royal Society, Queensland*, xxiv., 195.

TABLE IV. (continued).

Temperature observed. Degrees below zero.	Cc. of added water in 1 litre of sample.	Temperature observed. Degrees below zero.	Cc. of added water in 1 litre of sample.
0°482	123°6	0°382	305°4
0°481	125°4	0°481	307°3
0°480	127°3	0°380	309°1
0°479	129°1	0°379	310°9
0°478	130°9	0°378	312°7
0°477	132°7	0°377	314°5
0°476	134°5	0°376	316°4
0°475	136°4	0°375	318°2
0°474	138°2	0°374	320°0
0°473	140°0	0°373	321°8
0°472	141°8	0°372	323°6
0°471	143°7	0°371	325°4
0°470	145°4	0°370	327°3
0°469	147°3	0°369	329°1
0°468	149°1	0°368	330°9
0°467	150°9	0°367	332°7
0°466	152°7	0°366	334°5
0°465	154°5	0°365	336°4
0°464	156°3	0°364	338°2
0°463	158°2	0°363	340°0
0°462	160°0	0°362	341°8
0°461	161°8	0°361	343°6
0°460	163°6	0°360	345°4
0°459	165°4	0°359	347°3
0°458	167°3	0°358	349°1
0°457	169°1	0°357	350°9
0°456	170°9	0°356	352°7
0°455	172°7	0°355	354°5
0°454	174°5	0°354	356°4
0°453	176°4	0°353	358°2
0°452	178°2	0°352	360°0
0°451	180°0	0°351	361°8

The indiarubber cork has two perforations for carrying thermometer and stirring rod respectively.

The first thermometer we used was a Beckmann graduated in one-hundredths. The special thermometer devised by Winter for this work was subsequently obtained from Paris, but we found the Beckmann easier to read. For the last year a thermometer graduated in one-hundredths, a degree covering 8·5 cm. of the stem, and specially made for us of normal glass by the V.F.L., has been used and gives splendid results. The trouble of having to occasionally readjust the mercury of the Beckmann has been avoided, while the true zero-point, which is determined afresh at least once every day on which the thermometer is used, has not varied more than 0·02° C. A small telescope, H, is used for reading the thermometer. The telescope is mounted on the stand in the usual manner. The stirrer, K, is a brass rod 2 mm. in diameter, the spiral part being partly flattened out and armed with four small points of wire, to break up the ice formed in standardising.

In practice, 50 cc. of each milk to be tested is put into a tube fitted with a cork, and the tubes are put into crushed ice and allowed to remain there (generally standing in the ice chest) until required. By this means the freezing of each sample is started close to 0° C. While the samples are cooling the freezing mixture is prepared. The ice is conveniently prepared from the ice block by means of the usual ice plane. Alternate layers of ice and salt (3 : 1) are added until the porcelain beaker is filled. When about half-filled an empty "milk" tube is put into the middle of the beaker and the mixture packed around this tube. On removing the empty tube when the beaker is filled, there is no difficulty in inserting the tube containing the milk sample. After filling the beaker, the shelf is put in position on the rests and the beaker put on it. A tube containing a sample is then put through the hole in the top of the stand into the freezing mixture. The indiarubber cork is inserted, carrying the thermometer and the stirrer. The thermometer has been so adjusted that the bottom of the

thermometer is about 2 cm. from the bottom of the tube when the cork is in position.

The stirrer is now worked up and down continuously at the rate of from one to two complete movements per second, to prevent the formation of a solid block of frozen milk in the tube as the temperature falls. As a rule the mercury will rapidly fall to a point below the true freezing-point of the milk (surfusion of the milk), and then rapidly rise and become almost stationary; the highest point of the rise after the fall will be found to be very close to the true freezing-point. When the tube has become partly filled with finely broken up frozen crystals—experience with the method soon enables one to judge of the correct proportion of crystals to have in the liquid—the porcelain beaker containing the freezing mixture is removed by withdrawing the shelf C and lowering the beaker and the hand put round the tube G, so that its warmth may cause a rise in temperature, the stirrer being worked very gently until there is a rise of about two-hundredths on the thermometer scale. The hand is now removed and the milk well stirred, so as to surround the thermometer bulb with crystals of frozen milk.

The stirring is stopped and the temperature observed—the mercury will slowly fall, and when it becomes stationary the reading is taken, but should not be taken as final unless it remains constant for at least two minutes.

The position on the thermometer scale of the freezing-point of water is determined in exactly the same way as in the case of milk, distilled water being first placed in one of the tubes F, and cooled in a mixture of ice and water. Particular care, however, must be taken to break up the ice formed and to prevent the formation of a shell of ice round the sides and bottom of the tube. The fine ice should extend from the surface to the bottom of the thermometer bulb to ensure a good reading. It is much easier to determine the freezing-point of milk than that of water, owing to the fact that "milk" crystals are easily kept small, while water always tends to freeze in one lump. The difference between the freezing-point of the distilled water and that of the milk on the thermometer gives the freezing-point of the milk.

For deducing the proportion of added water from the determined freezing-point Table IV., extended from Winter's, is used.

RADIUM.*

(Continued from p. 266).

APPENDIX I.

Our Radium Resources.†

By CHARLES L. PARSONS, Chief of the Division of Mineral Technology, Bureau of Mines.

THE "wonders of radium," both fact and fable," have been treated so extensively in the scientific and public press that it is not my intention nor is it at all necessary to repeat them here. Rather it is my wish to-day to present to a body of men interested in the development of American mining the present commercial situation as regards radium and its ores, and to point out, so far as I may, some of those future developments that already begin to be more or less distinctly visible.

A bulletin on the radium, uranium, and vanadium situation, by R. B. Moore, physical chemist in charge of the Denver office of the Bureau of Mines, and K. L. Kithil, mineral technologist of the Bureau, will appear within a few weeks and will contain much detail of interest to the mining industry. Last April an advance

* Report No. 214, presented to the House of Representatives, U.S.A., at the 63rd Congress.

† Paper presented before the American Mining Congress, Philadelphia, October 23, by permission of the Director of the U.S. Bureau of Mines. Reprinted from the *Journal of Industrial and Engineering Chemistry*, vol. v., No. 11, November, 1913.

statement, authorised by the Director, regarding this bulletin, brought out particularly the fact that practically all of the carnotite ore mined in the world in 1912 was shipped abroad, and that this country was furnishing annually nearly three times as much radium from its Colorado carnotite deposits as all the rest of the world put together. It was further pointed out that this material has been bought by European buyers at a price entirely incommensurate with its radium value and that efforts should be made to keep at home both the radium itself and the profits of its manufacture; also that too much stress could not be laid upon the extensive waste of valuable radium ore thrown on the dumps of mines and prospects—much of it under such conditions that it could never be recovered.

The publication of this statement has already resulted in an increase of at least 33 per cent in the price of carnotite ore, and European buyers are awakening to the fact that they must pay to the American miner a price nearer the actual value of his ore. Also, a much lower grade of ore is now marketable, for whereas six months ago ore containing 2 per cent uranium oxide was the lowest grade accepted by European buyers, agents of these buyers are now asking for and actually purchasing ore containing no more than half this content of uranium. Furthermore, the operators are taking more care in separating their low-grade ore from the gangue and in protecting it from wind and weather. Moreover, old dumps are being sold, and ore that a few months ago was thrown aside as valueless will be recovered from them.

In this paper I shall refer to other facts contained in this bulletin and shall mention some new developments having a direct bearing upon the American radium industry which have taken place since the manuscript was sent to the printer.

As is well known to all of you, the popular belief has been that the chief source of radium is the mineral pitchblende, especially that obtained from the mines now under the control of the Austrian Government at Joachimsthal, Bohemia, and pitchblende is the richest and most eagerly sought uranium radium ore. Outside of the ore in Austria, the only pitchblende deposits of any size are those in Gilpin County, Colorado, from which some 30 tons more or less have been procured since the mineral became valuable as a source of radium. The Denver papers recently announced that these pitchblende-bearing mines have been acquired by Alfred I. duPont, of Wilmington, Delaware, and it is greatly to be hoped that their exploitation under his direction will yield an increased supply of this valuable mineral. It is not, however, so generally recognised that the mineral carnotite, which outside of the United States occurs only in low-grade ores mixed with ilmenite in the Olray district of South Australia and as a calcium carnotite (communicated by W. F. Hillebrand) under the name of Tyuyamyunite in Ferghana, Russian Turkestan, is by far the more important source of radium. From the most authentic sources it can be definitely stated that the Australian and Russian deposits do not compare in extent or richness with our own. The American carnotite is accordingly the largest source of radium at the present time, and at least four times as much radium was mined in America in the form of carnotite in 1912 as has been produced from Colorado pitchblende since it was first discovered in that State.

Outside of carnotite and pitchblende, the only other known source of radium is the mineral autunite. The autunite deposits of Portugal have probably furnished a few milligrams of radium to commerce, and from the Mt. Painter deposits in South Australia a few tons of autunite-bearing ores have been shipped to London.

American carnotite is found chiefly in Montrose and San Miguel counties, Colorado, and in Utah north-west of these counties. The Utah deposits are at Green River, Table Mountain, Richardson, Fruita, Moab, and some sixteen miles south-east of Thompsons. The ores of these deposits are of a lower grade than those of the Paradox

Valley, but they are nearer to the railroads and transportation costs are much less. The Green River deposits have apparently become regular producers. In Colorado, prospects have been opened at Coal Creek, 14 miles north of Meeker and at Skull Creek, 65 miles west of Meeker; but the richest of all American carnotite localities and indeed the richest known radium-bearing region in the world is that of the Paradox Valley, Colorado, extending from Hydraulic on the north to the McIntyre district on the south.

Geologists are now in the field making a special study of these carnotite ores with special reference to their occurrence and origin, of which altogether too little is now known. In the Paradox region the deposits seem to lie invariably just above the fine-grained La Plata sandstone. This rock is usually exposed high on the sides of the canyons, some of which are excelled in extent and in natural beauty by only the Grand Canyon itself. In a few instances, as at Long Park and Club Ranch, the deposits are only a few feet under the surface, the higher formations having been eroded; but for the main part, the stratum in which the carnotite occurs, when not entirely eroded, is deep below the surface of the mesa. Accordingly prospecting is mainly carried on along the sides of the canyons, and where vanadium and uranium stains are seen upon the rock the prospector blasts his tunnel in the hope of developing a pocket of the ore. The fact that the ore occurs in pockets renders prospecting uncertain, and there appears to be no present hope of insuring a successful search for pockets that are not exposed or do not happen to be near the surface. Although it is probable that many other pockets of carnotite occur at the same geologic horizon, their discovery, except where the ore-bearing stratum has been exposed by erosion, appears at present to be an almost hopeless task. The eroded sides of the canyons have been prospected again and again, but new claims are still being opened and are being sold by the prospector to the larger companies or operators who mine the ore. In such a sale the prospector and the purchaser both take a decided risk, for at present no method is used to determine the extent of the ore in the pocket other than the "prospector's hole."

As few of the prospectors of the west are acquainted with carnotite and pitchblende, the following description of the ores has been issued from the Denver office of the Bureau of Mines and is sent to all who make inquiry.

"In reply to your letter for information concerning radium ores, the following facts may be of interest:—

"Radium is found associated with uranium minerals only. Wherever uranium exists, radium is also found in the mineral; and where there is no uranium, radium has never been found. Uranium and therefore radium are found in this country in carnotite and its associated minerals, and in pitchblende. Carnotite is a lemon-yellow mineral usually found in pockets in sandstone deposits. The mineral may be in the form of light yellow specks disseminated through the sandstone, or as yellow incrustations in the cracks of the sandstone, or may be more or less massive, associated with blue, black, or brown vanadium ores.

"Pitchblende is a hard, blue-black ore that looks something like magnetite, but is heavier. It is found in pockets and veins in igneous rocks. This mineral is not nearly as widely distributed as carnotite. Occasionally it is found associated with an orange mineral called gummite.

"The best way to test these ores is to wrap, in the dark, a photographic plate in two thicknesses of black paper. On the paper lay a key, and then, just above the key, suspend two or three ounces of the ore, and place the whole in a light-tight box. Pressure of the ore on the key and plate should be avoided. After three or four days, develop the plate in the ordinary way; and if the ore is appreciably radio-active, an image of the key will be found on the plate.

"The U.S. Bureau of Mines, 502, Foster Building, Denver, Colorado, will be glad to receive any samples of

ores giving promise of containing radium and associated rare minerals, as indicated by the test above described. Though it cannot undertake to make chemical analyses or assays of such minerals for private parties, it will indicate the advisability of further examination."

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 19, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"Note on the Circulation of the Atmosphere." By A. MALLOCK, F.R.S.

"Origin of the Indo-gangetic Trough, commonly called the Himalayan Foredeep." By Col. Sir SIDNEY BURRARD, F.R.S.

"Approximately Permanent Electronic Orbits and the Origin of Spectral Series." By G. W. WALKER, F.R.S.

In this paper an endeavour is made to find a basis of explanation of spectrum series in terms of strict electro-dynamics. The illustrative system consists of a spherical nucleus radius a , with a positive electric charge E and a fixed magnetic moment μ . It is constrained to be fixed, and may be regarded as corresponding to a comparatively massive atom. A single corpuscle with a negative charge e , and mass m is free to move under the influence of the forces exerted on it by the nucleus.

When the effect of radiation is neglected circular orbits are shown to be possible. The circumstances, stability, and range of these orbits are examined in detail, both for orbits outside and inside the nucleus. Only the inside orbits appear to have a bearing on the problem in hand.

It is found that there is a class of circular orbits in each of which the angular momentum of the corpuscle has the same value. This result has already been obtained by Conway, who sought to identify the value with Planck's unit. It is here shown that these orbits occur only if the charge of the nucleus is concentrated mainly at the surface, or if the material of the nucleus has a large dielectric ratio.

In any case, to get a suitable frequency the angular momentum is but a small fraction of Planck's unit. The frequency is given by the form—

$$\gamma = A - B(r/a)^2,$$

where r is the radius of the sphere on which the corpuscle lies and A and B are consonants proportional to $\frac{e}{m} \frac{\mu}{a^3}$, the numerical factors depending on the way in which the magnetic moment is distributed.

Another class of circular orbits exists. They lie in the equatorial plane of the nucleus and have different angular momenta. The formulæ although possessing the same general features are not so simple as those for the Conway orbits.

The effect of radiation is next considered. The motion of the corpuscle gives rise to radiation disturbance inside and outside the nucleus, while the nucleus produces radiation in the manner proved by Lamb. The disturbance can be analysed into terms of electric and magnetic type. In each case a series of values of r/a are found for which the reaction on the corpuscle becomes very small, and so it is argued that the corpuscular orbit for which r/a has one of

these values is comparatively stable, and gives a spectral line. Following Lamb in supposing that the dielectric ratio is great, we find that from the Conway orbits with magnetic type of disturbance we get the recognised Balmer formula, while with the electric type of disturbance we get a series closely resembling the Rydberg formula.

Only one orbit is permissible within the nucleus at any specified time, but the whole series may be exhibited in the course of an optically long time with a large number of such nuclei.

In addition to these series we ought to get Lamb's series from the nucleus, but quite consistently with the theory they may be in the infra-red or the ultra-violet. In order to fit the formula of Balmer type with the hydrogen series, and taking $e/m = 1.7 \times 10^7$, $\mu = 1.8 \times 10^{-21}$ the radius of the nucleus required is about 2×10^{-10} cm.

"Spectroscopic Investigations in connection with the Active Modification of Nitrogen. IV. A Band Spectrum of Boron Nitride." By W. JEVONS.

1. The interaction of active nitrogen and boron trichloride or methyl borate develops a band spectrum extending from $\lambda 6371$ to at least $\lambda 2140$, with well-defined heads degrading throughout towards the red.

2. The new spectrum consists mainly of two distinct systems, in the less refrangible of which each band consists of four heads forming two close doublets. The more refrangible system has single heads, and thus resembles the silicon nitride spectrum described in a previous paper.

3. The wave-lengths of the heads have been measured, and the wave-numbers in each system have been classified and represented by formulæ in the usual manner.

4. Chemical and spectroscopic evidence has established that the origin of the spectrum is boron nitride. Boron, carbon, and silicon compounds are thus alike in developing nitride spectra in the nitrogen afterglow.

5. The boron nitride bands, like those of cyanogen, are produced in the electric arc spectrum where they occur together with bands of the oxide.

"Additional Note on the Production of High Permeability in Iron." By Prof. ERNEST WILSON.

It has been shown that if stalloy in laminated ring form is subjected to a magnetising force due to a direct current whilst it is cooling through the temperature at which it regains its magnetic properties, and is at the same time shielded from the influence of the earth's magnetism, the permeability recovered at atmospheric temperature has a maximum value of over 10,000 when the magnetic induction was of the order of 6000 C.G.S. units.

It had been shown previously that high values of the permeability can be obtained without the use of a special magnetic shield when iron has impressed upon it a magnetising force, due to an alternating current, during the time that it cools through the temperature at which it regains its magnetic properties. As, however, in the last-mentioned case, an iron tube was used to enclose the specimen and became heated with the specimen, it was thought desirable to discover whether the high value of the permeability can be obtained when there is no question of magnetic shielding. In the present experiments the specimen of stalloy in ring form was allowed to cool inside a sealed fire-clay crucible when subjected to a magnetising force of 13 C.G.S. units, and at atmospheric temperature a permeability of over 10,000 was again obtained.

Further experiments have been made with stalloy in the form of straight strips. The specimen, which consisted of a number of strips side by side, was wound with a magnetising coil and then placed inside an iron tube. On allowing it to cool through the temperature at which magnetic quality is regained, when subjected to a magnetising force due to a direct current, the improvement in maximum permeability, when at atmospheric temperature, was small, and had apparently disappeared when re-tested at the maker's works.

ANNIVERSARY MEETING,

November 30, 1914.

THIS being St. Andrew's Day, the anniversary of the Royal Society, the President, Sir WILLIAM CROOKES, delivered his annual Address as follows :—

Since the last Anniversary the Royal Society has lost by death sixteen Fellows and six foreign Members. It is my sad duty to express our united sorrow at the loss.

Sir David Gill—the greatest practical astronomer of our times and a scientific worker of peculiarly high ideals—died in London early in the present year after long illness. Sir David Gill's work as Her Majesty's Astronomer at the Cape of Good Hope brought him great distinction. His energy was superabundant and his enthusiasm unbounded. Owing to his efforts the observatory at the Cape has become one of the leading observatories of the world. He attracted a keen band of workers who were encouraged to publish the results of much valuable work achieved under his guidance. He also inspired many younger astronomers, some of whom have now come to the front. His keen appreciation of accurate work, his engineering skill which enabled him to eliminate small systematic errors, made his parallax work with the heliometer the high water mark of practical astronomy. His work was also directed to great astronomical problems which he attacked with enthusiasm and persistency. The geodetic work which he directed ranks with the great Russian and Indian works. His "History and Description of the Royal Observatory, Cape of Good Hope," contains a remarkable record of his wonderful powers of organisation, his extraordinary determination in overcoming difficulties, and his self-confidence—fully justified by the outcome of his projects. His best known researches were on stellar and solar parallax, and on the determination of the mass of the moon, and of Jupiter. Gill's singlemindedness and strong personality won him many friends and admirers who sincerely mourn his death.

The death of Professor John Henry Poynting has deprived the scientific world of a physicist to whose work it is difficult to do justice in a brief report. Appointed Professor of Physics in Birmingham in 1880, Poynting became a Fellow of the Royal Society in 1888. In 1905 he was elected President of the Physical Society, and was awarded a Royal Medal by the Royal Society for his researches in physical science, especially in connection with the gravitation constant and the theories of electrodynamics, and radiation. His determination of the Newtonian constant of gravitation by the process known as "weighing the earth" was published in 1891. The theorem, known by his name, connecting mechanical motion with electric and magnetic forces is a fundamental generalisation—and his work, both theoretical and experimental, upon radiation pressure was hardly less important. He proved that a beam of light behaves in all respects like a stream of momentum, and he evolved a method of determining the absolute temperature of the sun, the planets, and of space. He was the author of a well-known series of text-books of physics, written in collaboration with Sir J. J. Thomson; he also wrote some interesting popular books on scientific subjects. His position as Dean of the Faculty of Science at the University of Birmingham brought him into intimate contact with many students who will inevitably remember his name with veneration and affection. In Professor Poynting we have lost a man of delightful personality and remarkable originality.

Professor George M. Minchin, who died in March, was a man of great versatility who won renown in more than one branch of natural knowledge. For many years he was Professor of Mathematics at Cooper's Hill Engineering College—and he was the author of original and widely-used works on Statics, Kinematics, and Hydrostatics. He was a polished writer both of prose and verse, and was the master of a clear and graphic style. His pioneer experimental work on photo-electricity and selenium cells was

begun in 1877, when he discovered that electric currents are produced by the action of light upon silver plates coated with emulsions of bromide or other silver salt; the cells he called "impulsion cells," which had their sensitiveness to light altered by slight impulses or taps, embodied the principle of the coherer used for the reception of the Hertzian waves. He afterwards observed that similar results could be obtained by using two selenium-coated aluminium wires dipped in certain solutions; and in 1908 he described in a communication to the Royal Society further researches on new forms of the photo-electric cells, and on "seleno-aluminium bridges," which consisted of two aluminium plates separated by a thin flake of mica, and having a layer of sensitive selenium across one end of the mica and the adjacent portions of the aluminium plates. He used his cells to obtain measurable electromotive forces from the light of stars, and thus determined the relative intensity of the light of some of the fixed stars and planets. The results of his investigations agreed closely with those of photometric measurements of stellar magnitude. When Cooper's Hill College was closed Professor Minchin went to live at Oxford, where he remained until his death. He was elected a Fellow of the Royal Society in 1895.

The death of Sir Joseph Wilson Swan in his eighty-sixth year has deprived the scientific world of a distinguished investigator—and me personally of an intimate and valued friend. Sir Joseph Swan had a mind of extraordinary fertility of invention. At the same time he was endowed with an unusual amount of business capacity—a fortunate combination of qualities rarely found.

In his young days he was specially interested in photographic research. He was the discoverer of the first commercially practicable process of carbon printing, which he patented in 1862. He discovered the method of making extremely rapid dry plates, which revolutionised photography; and he also invented and patented the bromide printing process. Another field of research in which he won renown was the application of electricity in illumination. As early as 1860 he had constructed an electric carbon filament glow-lamp which he subsequently improved, finally arriving at the form which until quite recently was universally used. He discovered a valuable method of rapid deposition of copper, and also devised improvements in the construction of secondary batteries. His distinguished services to Science were recognised by the Royal Society, who elected him to its Fellowship in 1894, and ten years later awarded him the Hughes Medal, by the Society of Chemical Industry which bestowed upon him a gold medal, and by the Royal Society of Arts which awarded him the Albert Medal in 1904. By his discoveries and inventions Sir Joseph Swan did much to benefit what we perhaps mistakenly call "civilisation"; the practical value of his investigations, more particularly in the applications of Electricity, is unequalled in the history of Science.

Dr. George James Burch, who had been elected a Fellow of the Royal Society in 1900, passed away in March this year. Dr. Burch for many years was Professor of Physics at University College, Reading; he was also a University Extension Staff Lecturer at Oxford—where he lived. His early investigations were connected with electro-physiology, and he discovered a method of analysing electrometer curves, a description of which he published in 1890. His later years were devoted to the study of the physiology of vision; he published an interesting memorandum on Sight Tests, as well as a book describing the practical work done under his direction at the Physiological Laboratory at Oxford. In this book the highly original tests and exercises he evolved were described. His knowledge of visual physiology was unique and he achieved an eminent degree of success in the subject which he made specially his own. In his keen prosecution of research he was unsparing of strength and energy; it is said that in order to study colour blindness he made himself temporarily colour blind by exposing his eyes to the sunlight in the focus of a burning glass behind different coloured glasses.

In February the death occurred of Horace Bolingbroke Woodward, who, from 1867 to 1908, had taken an active part in the Geological Survey. He was in charge of the work in England and Wales for the last seven and a-half years. Woodward's knowledge of British Geology and especially of stratigraphical geology was profound. He published many memoirs on geological subjects, and he was the author of a valuable and original work on the Geology of England and Wales. He became a Fellow of the Royal Society in 1896, and served on the Council of the Geological Society for several years, being Vice-President from 1904 to 1906. He was an indefatigable worker and his writings were characterised by the great stress he laid upon accuracy in the minutest detail. He also had a gift for writing in an interesting and non-technical style which made a special appeal to the general reader. Although he was forced to retire from the Geological Survey some time before his death, he continued his literary work as long as strength would allow—and almost to the very end of his life he was engaged in preparing the statistical part of a Survey Memoir on Water Supply. His many friends, and especially those who were associated with him on the Survey, will long remember him with grateful affection for the help and sympathy he willingly lavished, and for the example he set of untiring industry and enthusiasm.

Dr. Albert C. L. G. Günther had a distinguished career as a zoologist, and the progress of the science owed much to his investigations. He was appointed Keeper of the Department of Zoology of the British Museum in 1857—under his charge the department was brought to a high state of efficiency. He published many communications in the *Philosophical Transactions* and the *Proceedings* of the Zoological and Linnean Societies, and he founded the "Record of Zoological Literature," editing the first six volumes. In 1878 he received a Royal Medal from the Royal Society for his work in zoology and especially for his researches in herpetology and ichthyology.

The death of Dr. Walter Holbrook Gaskell in the full tide of his powers is a heavy blow to his friends and a great loss to the scientific world. Dr. Gaskell exercised a powerful influence upon the development of physiological science. His early research work in physiology was inspired by Michael Foster and by Karl Ludwig, of Leipzig. His work upon the mechanism of the beat of the heart was that of a pioneer of great originality and intrepidity. His investigations of the sympathetic nervous system were of fundamental importance, and his generalisations were far-reaching and based upon keen observational powers. His views upon morphological questions were original and in some respects at variance with those of other authorities. His later years were spent in accumulating material in support of his theories and in expounding them in fuller detail. He was a keen and vigorous worker in physiology. He can ill be spared and his loss will long be severely felt.

The death of Dr. Philip Henry Pye Smith after a long and busy life occurred in May. Owing to ill-health he passed the later years of his life in retirement. He will be greatly missed by the wide circle of friends and acquaintances who were attracted by his geniality and kindness, his wide interests and profound knowledge. He led a life of great public activity and received many honours from Scientific Societies and Universities. He served on the Council of the Royal Society in 1891—1892; besides his work as physician to Guy's Hospital he found time to edit Fagge's work on the "Principles and Practice of Medicine." He also published many papers on medical subjects. He was one of the great authorities upon Skin Diseases, and was keenly interested in the history of Medicine. He was an admirable lecturer; countless students have reason to be grateful to him for his careful training and his insistence upon the importance of accurate observation and cautious deduction.

Geological Science suffered a severe loss in the death in August of Alfred John Jukes Browne. At the end of a

successful University career at Cambridge, where he did excellent work under Professor T. G. Bonney, Jukes Browne joined the Geological Survey. Afterwards he specialised in the palæontological zones in English chalk strata. He also investigated the oceanic deposits of Barbadoes, and he was the author of highly successful and widely-used text-books on general Geology. He received the Murchison Medal of the Geological Society in recognition of his valuable services. Although severely hampered throughout the greater part of his life by ill-health, and for the last twelve years forced to live a secluded and quiet life, his work will long survive, and his name be remembered as that of one of the most distinguished Geologists of his day.

In the Right Hon. Joseph Chamberlain and Viscount Cross the Royal Society has lost two distinguished members. They put forth no claim to be regarded as scientific specialists; but each was inspired to turn some page of "Nature's infinite Book of Secrecy."

The narrative of the career of Sir John Murray, who also died this year, is full of interest and romance. Owing to his tireless activity and strong individuality he was responsible for an amount of brilliant work hardly equalled by that of any other investigator in the same sphere. His early scientific training, during which he refrained from specialising in any particular branch, but studied all subjects which interested him, laid the foundation of his extraordinarily wide knowledge. His adaptability and resource were qualities invaluable to his colleagues upon the *Challenger* Expedition, to which he was appointed Naturalist. He proved himself to be a remarkably acute observer of strong deductive powers and sound judgment; he had the courage of his conviction and was never chary of attacking established views when he believed he could prove them to be incorrect. His theory of the origin of Coral islands, which after much controversy was finally almost universally accepted, was from the geological point of view revolutionary. His investigation of the freshwater lochs of Scotland is a remarkable piece of work. He was keenly interested in the exploration of the Sea, and made many voyages on his own yacht for the purpose of oceanographic investigation. He had a strong business instinct, and although throughout the whole of his long career he was deeply imbued with a love of Research for its own sake, he was always capable of quickly perceiving the commercial applications of his conclusions. Upon several occasions he gave valuable practical advice to the Government.

The late Lord Strathcona and Mount Royal—elected a Fellow of the Royal Society in 1904—will long be remembered as one who gave his whole life and all his powers to the extension of the British Empire and the strengthening of the bonds of its union. His indomitable courage in the early dangerous and difficult days which he spent in Labrador and on the shores of Hudson's Bay, his foresight and determination in carrying out the project of the Canadian Pacific Railway, admirably revealed the temper of the man. The memory of his splendid patriotism and generosity will live long after him.

In June the death occurred of Joseph Reynolds Green—an active worker in physiological and botanical research and a prolific writer on these subjects. He made a special study of enzyme action, and was the discoverer of lipase in the germinating seed of the castor oil plant. His writings are characterised by great lucidity and accuracy, and his contributions to botanical science are of considerable importance.

Another name must be added to the heavy list of losses sustained by science during the past year—namely, that of Alexander Ross-Clarke, in charge of the Trigonometrical Operations of the Ordnance Survey from 1854 to 1881, and whose knowledge of geodesy was unsurpassed by that of any man of our time. His genius for mathematical calculation excites keenest admiration; his treatise on "Geodesy" is universally admitted to be the best book on the subject.

Among the Foreign Members of the Royal Society whom death has recently removed from our midst are Prof. A. Weismann, L. Hermann, Dr. H. Kronecker, Prof. E. Suess, Dr. G. W. Hill, and Mr. Silas Weir Mitchell.

Professor Ludimar Hermann, of the University of Königsberg, was the author of the "*Handbuch der Physiologie*," and for many years was editor of the *Jahresbericht über der Fortschritte der Physiologie*.

Professor August Weismann, of the University of Freiburg, received the Darwin Medal of the Royal Society in 1908. He contributed largely to the study of Evolution and was one of the earliest writers in support of the Darwinian theory.

Dr. Kronecker was a tireless worker in physiology. His researches at the Berne Physiological Institute won for him a truly world-wide reputation. He was the author of valuable monographs upon the physiology of the muscles and nerves.

The death of George William Hill removes from our midst one of the leading exponents of nineteenth century Celestial Mechanics. The two papers which contained his chief researches in the Lunar theory have, at the hands of Poincaré, Sir George Darwin, and others, created a new method of treating Lunar problems and have also led to the formation of a new theory and tables of the Earth's moon. The theories of Jupiter and Saturn with tables for these planets—which he completed in 1892—have superseded all previous work. His papers in four volumes are published by the Carnegie Institute of Washington. He possessed unusual intuition—another name for Genius—into the possibilities of the subjects he treated, and the originality of his methods was one of their most distinctive features.

Professor Edward Suess was a geologist of great eminence whose position amongst exponents of the science was unique. His monumental work on the "*Face of the Earth*" has been aptly described as the culmination and crown of the geology of the nineteenth century. It was Suess who brought together and collated the observations of all who have studied the form of the earth—and in addition much original work in both stratigraphical and palæontological geology was due to him.

Dr. Silas Weir Mitchell died in January last in his eighty-fifth year, his mental and bodily vigour continuing to the end. He was one of the foremost neurologists of the day, and his numerous books on nervous diseases made his name a household word in the profession. Moreover, he achieved a remarkable success in the domain of fiction, some of his novels taking a foremost place.

Probably at no time in its history has the financial responsibility of the Royal Society been more perplexing than it is to day. At the last Anniversary Meeting the President, Sir Archibald Geikie, referred to the annual expenditure on the National Physical Laboratory. He pointed out that should there be any serious falling off in receipts—such as might be caused by an interruption or stagnation of industrial enterprise—there would necessarily be a serious deficit, and that it would be impossible promptly to reduce the working expenses—at that time met by the receipts.

The financial strain foreshadowed by my predecessor has now befallen us. It is, however, to be hoped that, in view of the national character of the Laboratory, of the great services which it is rendering to the nation—services which are of extreme importance at the present crisis,—the Government may see fit to come to our assistance, so as to enable the Society to continue the work of this great Institution—a work which the Society's own resources will not enable it to do in existing circumstances. Those resources must of necessity have a great strain thrown on them in other directions, for we have now to face heavy liabilities in connection with our own "*Catalogue of Scientific Papers (1880–1900)*" and the preparation of the "*International Catalogue of the Scientific Literature of the Present Century*." On the foundation of the latter the

Society undertook to be responsible for the completion of the former. The cost of this has, owing to the vast increase of scientific literature at the close of the last century, proved to be largely in excess of the sum provided for its production mainly by the generosity of the late Dr. Ludwig Mond; and thus the necessary funds have had to be supplied by the Society itself, as at the present time it would be out of the question to appeal for further donations for this object. On the other hand, while it is certain that, owing to the World upheaval, a large part of the subscriptions from Continental nations, by which the cost of the production of the International Catalogue is defrayed, will not be forthcoming, the Society remains liable for the expense of the issue now in course of publication—an expense which must be large.

At the time of our greatest need we are confronted with the possibility of a serious diminution in income. The strengthening of the hands of our Government has rightly been regarded as having the first call on those in a position to render financial aid. Like every private individual the Royal Society must limit its expenditure and practise economy. On the other hand, we have imperative responsibilities and a duty to the nation which cannot be shirked. We dare not allow ourselves to slacken in our devotion to Research—but the fact remains that our need of money is greater now than ever. Our special object is to vivify and stir the spirit of philosophic inquiry and of scientific glory, at a moment when another kind of "*Glory*" transfixes the whole of the civilised—or shall we say uncivilised world? I will quote from Sir Humphry Davy's Discourse on the occasion of his taking the Chair of the Royal Society for the first time in 1820:—"Let us then labour together and steadily endeavour to gain what are perhaps the noblest objects of ambition—acquisitions which may be useful to our fellow creatures. Let it not be said that at a period when our Empire was at its highest pitch of greatness, the Sciences began to decline; let us rather hope that posterity will find in the *Philosophical Transactions* of our own days proofs that we were not unworthy of the times in which we lived." Science ought to be one of the great bonds of union and peace between Nations. Surely it would be a disaster to the whole world if the usefulness of the Royal Society were to be restricted by mere lack of funds. Many enquiries of vast importance have not received the support they deserved from the Royal Society solely owing to want of funds. To-day money is diverted to other urgent uses. It is nothing short of scientific tragedy that learned Societies are for the moment overlooked. It is the duty of those whom Davy spoke of as having been honoured with the rank of Generals in the army of scientific workers, to keep before the eyes of the public the urgent need of money for Science, and the colossal importance of scientific work for the welfare of the nation. We are emphatically the Trustees of the Future.

At a time like the overwhelming present, when our existence is at stake, it behoves those of us who cannot actively share in the great upheaval to take stock of our position among the nations of the civilised world. It is our duty, without morbid regret for the past, or craven fear of the future, to think of our own aims, and to reflect upon the aims of our adversaries as far as we are able to understand them.

In 1896 the Rumford Medal of the Society was given in duplicate to Professor Röntgen and to Dr. Philipp Lenard, Professor of Physics at Heidelberg. Professor Röntgen is stated by a Berlin paper not to care to retain his Medal and has given it to the Red Cross. Dr. Lenard is credited by a German paper with the following savage outburst:—

"Down, then, with all considerations for England's so-called culture. The central nest and supreme academy for all hypocrisy in the world, which is on the Thames, must be destroyed if the work is to be done thoroughly. No respect for the tombstones of Shakespeare, Newton, and Faraday!"

The recent manifesto of the German Professors is a monstrous utterance, and in the words of a German paper is a grave symptom of national insanity.

Reading between the lines I think we may see that the signatories recognised they have been betrayed by facts, and they are forced to make an appeal to theory. So also we believe they will find their reliance on brute force is doomed to end in failure. On the other hand, we look beyond the "Sacrifice of blood and treasure" to the vindication of an idea, the establishment of a principle. The dignified reply of the English Scholars to the manifesto of the German Intellectuals is confined to a recital of facts.

The united Universities of France have addressed to the Universities of the Neutral Nations a noble and imposing document in which the claims of Germany are answered in a manner beyond all question.

The Royal Society is always cosmopolitan in spirit, and we should be unworthy of our heritage could we not, even at this desperate moment, take a dispassionate view of events, and preserve a well balanced and rational attitude towards our contemporaries of German nationality.

Our senior Honorary Secretary, Sir John Bradford, whose absence we greatly regret, has recently gone to the front as Consulting Physician to the Forces. We are glad to congratulate him on filling a position of such vital service, and we wish him success in the strenuous work certain to fall to his lot.

The Report of our Council gives a full notice of important events of the past year. But there are some results of investigations to which I call special attention.

The work of Prof. W. H. Bragg and his son, W. L. Bragg, on the application of X-rays and crystal structure form a splendid "first fruits" of an entirely new field of crystallographic research. Mr. H. G. T. Moseley has recently studied photographically the X-ray spectra of many of the elements, and he furnishes some very interesting results relating to the connection between the spectrum and the atomic number of the element.

In the Bakerian Lecture on Series Lines in Spark Spectra, Prof. A. Fowler has a direct bearing on the constitution of the atom—confirming the theoretical work of Dr. Bohr. The peculiarities of the series of new lines produced by passing strong discharges through helium tubes containing hydrogen as an impurity, led to the search for other series of similar character, and experiments were performed with magnesium, calcium, &c., in which many new enhanced lines were obtained. It is interesting to notice that Bohr's theoretical formulæ for hydrogen and helium agree closely with the observed facts; if his formulæ are adopted, the mass of the hydrogen atom in terms of the electron is 1836 ± 12 .

The subject of the constitution of the atom has come into extreme prominence—great advances have been made—while much light has been thrown on the ultimate structure of matter. Years ago, during the persistent and systematic fractionation of yttrium, I explained that I had succeeded in separating the atoms of the so-called element into groups; these groups undoubtedly exhibited different phosphorescent spectra and presumably had different atomic weights—although from the chemical point of view all the groups behaved similarly. I concluded that, of the lines and bands of the compound spectrum of an element, some are furnished by certain atoms and some by others. I pointed out that this was not likely to be an isolated case; that probably in all so-called elements the whole spectrum does not come from all the atoms—that different spectral rays come from different atoms, which may be interpreted to mean that there are definite differences in the internal motions of the several groups of which the atoms of a chemical element consist. I ventured to suggest a possible explanation of these facts, based on the assumption that acting on the original *protyle* were two forces—one of the character of Time, accompanied by a lowering of temperature, while the other, swinging to and fro like a pendulum, and having periodic cycles of ebb and

flow, rest and activity, would be intimately connected with the force of electricity. I arrived at a presentation of the elements on a lemniscate path which seemed to me to throw some light on the question of their genesis. My researches seemed to show that the persistence of the ultimate character, the eternal self-existence, the fortuitous origin of the chemical elements, could no longer be regarded merely as probable.

Apparently bodies exist which possess close upon the same atomic weights and combine in definite proportions with other substances and yet exhibit certain minute differences. For these substances, which are capable of being isolated and identified, I suggested the name "meta-elements." Thus there appears to me to be a gradation of molecules of different ranks between the atom and the compound—and these aggregations of atoms in certain circumstances might well pass for simple elementary bodies.

In recent years the old ideas of the ultimate atom as a solid particle, spherical or otherwise, has slowly, almost imperceptibly, given way to the more rational conception of a minute planetary or "Saturnian" system of dazzling complexity; the conception is many minded, aided here and there by facts that failed to fall in with the old lines of thought. Among the most prominent men through which the new conception has come to light we have Kelvin, Stoney, Thomson, and more recently, headed by Sir Ernest Rutherford, a host of vigorous workers in the new science of radio-activity, who have built up a conception of atomic physics often "hard to be understood," but that probably is a move in the right direction. Sir Ernest Rutherford supposes the atom to be composed of a nuclear positive charge, exceedingly small compared with the sphere of action of the atom, and consisting of a number of unit charges. Surrounding this nucleus is an external shell in which a number of separate negative electrons are distributed. Professor Soddy—whose name is closely associated with that of Sir Ernest Rutherford—is one of the earliest workers in radio-activity, and has developed a theory of the chemistry of the radio elements based upon the periodic law and a modified form of lemniscate spiral where the existence of *pseudo* elements having slightly different atomic weight but identical chemical properties are set out. These "isotopic" elements occupy the same place in the Periodic Table. He has thus arrived, by a totally different path from the one I travelled, at the conception of an element having atoms of different weight though chemically identical. The theory has recently received some confirmation by the analyses of the lead that is found in the minerals pitchblende, thorinite, &c. In my own laboratory a spectroscopic examination of the lead from Cornwall pitchblende has shown traces of thallium not found in pure assay lead; the unexpected presence of this element may have some bearing on the slightly different atomic weight values recorded for the lead extracted from the radio-minerals.

Without risking a charge of being unduly optimistic, I think I may believe we are on the brink of striking developments in our knowledge of the structure of the elusive atom. Whatever may be the outcome of researches now prosecuted with so much zeal and success, I feel that Addison was speaking with the voice of prophetic Truth when, more than a hundred years ago, he said, "Every atom is a standing miracle, and endowed with such qualities as could not be impressed upon it by a Power and a Wisdom less than infinite."

With great pleasure I announce that the *Copley Medal* this year is awarded to Sir Joseph John Thomson, in recognition of the value of his researches in Physical Science. His early work in the investigation of electrical phenomena showed he possessed a high degree of experimental ingenuity and skill; by his study of the passage of electricity through gases he elucidated the nature of the negative electrical particles, thus providing an experimental basis for the atomic theories of the nature of electricity. His

treatise on the Conduction of Electricity through Gases won for him a world wide reputation as a physicist—to which subsequent work has added. To him is due the investigation of the nature of the positive carriers of the electric charge; his method of positive ray analysis puts a new and extraordinarily valuable tool into the hands of investigators. His experimental work has always been controlled and confirmed by theoretical considerations; his work at the Cavendish Laboratory at Cambridge has greatly extended our knowledge of the structure and nature of matter.

The *Rumford Medal* is awarded to Lord Rayleigh, in token of the Council's appreciation of the mathematical and physical work associated with his name. Lord Rayleigh has perhaps done more than any scientific man living to stimulate research; his work in the sciences of Heat and Radiation has paved the way for remarkable advances, both theoretical and experimental. The Copley Medal was given to Lord Rayleigh in 1899, but the Council wish to offer him some further mark of their recognition of the great value of the research which he still continues to pursue with such conspicuous success.

The two *Royal Medals* annually presented by the King have—with His Majesty's approval—been assigned to Prof. E. W. Brown and Prof. W. J. Sollas. Prof. E. W. Brown, who now occupies the chair of Mathematics at Yale University, devoted himself for many years to the study of the movements of the moon; and by incredible industry seven years ago he brought to a successful conclusion his investigation of this fundamentally important practical problem. He has recently further studied some phenomena which known gravitation causes do not explain, and he has extended his investigations to the General Theory of Orbits. His work in dynamical astronomy has been remarkably fruitful, and doubtless the years to come will add lustre to his already brilliant reputation.

The *Royal Medal*—awarded to a worker in Biological Science—this year has been conferred on Prof. Sollas, who is a pioneer in many fields, and has made many valuable contributions to our knowledge of geology, mineralogy, zoology, and ethnography. His monograph on Sponges is a classic on the subject. He has perfected a method of obtaining transverse sections of fossil organisms and thus he has obtained a knowledge of the structure of certain specimens which long have been the subject of dispute. We hope that Prof. Sollas will have many opportunities of extending his investigations which already have borne so much valuable fruit.

The recipient of the *Davy Medal* is Professor W. J. Pope who has made highly important discoveries in stereochemistry, and whose work has thrown much light upon the relation between chemical constitution and crystalline structure. In collaboration with Professors Perkin and Wallach Professor Pope has published the results of many experiments dealing with the isolation and investigation of optically active compounds of nitrogen, tin, selenium, and sulphur; he explains their activity by supposing that the radicles in the active compound are tetrahedrally arranged round a central atom as in carbon compounds. With Professor Barlow he has more recently been engaged in the establishment of a theory dealing with the connection between crystalline structure and chemical constitution. He has succeeded in reproducing the crystalline form of most substances of known composition, basing his work upon the assumptions of his theory—the experimental and theoretical results show a remarkable concordance. He has further suggested a theory of "valency volume" which is leading to important developments in the investigation of atomic volumes.

The *Darwin Medal* this year is awarded to Professor Poulton, in recognition of the value of his researches upon the curious phenomena of mimicry and protective resemblance in insects. Prof. Poulton has brought together a vast number of facts which confirm Darwin's theory on the subject and he has recently devised and organised a

remarkable series of breeding experiments with species of insects in order further to test his conclusions.

The *Hughes Medal* is this year conferred upon Professor J. S. Townsend, of the University of Oxford, for his work upon molecular conduction in gases, and upon the nature of the disruptive discharge. Prof. Townsend has made a brilliant investigation of the phenomena of conduction by the ionisation of gases by means of Röntgen and similar radiations. The study of the diffusion of the ions of gases led to very important conclusions about the size and nature of gaseous ions—and the theory of ionisation has been greatly extended by Prof. Townsend's work.

At the conclusion of the President's Address a Ballot was taken for the election of Officers and Council for the ensuing year. The following were elected:—

President—Sir William Crookes, O.M., D.Sc.
Treasurer—Sir Alfred Bray Kempe, M.A., D.C.L.
Secretaries—Sir John Rose Bradford, K.C.M.G., M.D., D.Sc.; Prof. Arthur Schuster, Sc.D., Ph.D.
Foreign Secretary—Dukinfield Henry Scott, M.A., Ph.D., LL.D.

Other Members of the Council—Sir Thomas Clifford Allbutt, K.C.B.; Prof. William Maddock Baylis, D.Sc.; Frederick Frost Blackman, D.Sc.; Henry John Horstman Fenton, Sc.D.; John Stanley Gardiner, M.A.; Archibald Edward Garrod, F.R.C.P.; William Bate Hardy, M.A.; James Hopwood Jeans, M.A.; George William Lamplugh; Prof. Augustus Edward Hough Love, D.Sc.; Prof. Raphael Meldola, D.Sc.; Sir John Thornycroft, LL.D.; Prof. John Sealy Townsend, M.A.; Alfred North Whitehead, Sc.D.; Charles Thomson Rees Wilson, B.Sc.; Arthur Smith Woodward, LL.D.

CHEMICAL SOCIETY.

(Continued from p. 281).

233. "The Constituents of the Flowers of *Matricaria chamomilla*." By FREDERICK BELDING POWER and HENRY BROWNING, jun. (*Trans.*, 1914, 2280).

The material employed for this investigation consisted of the flower-heads of *Matricaria chamomilla*, Linné.

In addition to a deep blue essential oil, which deposited a very small amount of umbelliferone methyl ether, the flowers were found to contain the following compounds:—(i.) Salicylic acid, together with, apparently, an octoic acid; (ii.) apigenin, $C_{15}H_{10}O_5$; (iii.) a glucoside of apigenin, which could not be obtained in a crystalline state; (iv.) umbelliferone methyl ether, $C_{10}H_8O_3$, and a crystalline product (m. p. 237–239°) which possessed the characters of a mixture of umbelliferone and a dihydroxycoumarin; (v.) choline, $C_5H_{15}O_2N$; (vi.) triacontane, $C_{30}H_{62}$; (vii.) a phytosterol, $C_{27}H_{46}O$; (viii.) a phytosterol glucoside, $C_{33}H_{56}O_6$; (ix.) palmitic, stearic, cerotic, oleic, and linolic acids, together with an indefinite mixture of volatile fatty acids. The flowers contained, furthermore, a quantity of sugar which yielded *d*-phenylglucosazone (m. p. 208°). The fatty and resinous material, from which some of the above mentioned substances were obtained, amounted to 5.9 per cent of the weight of flowers employed.

234. "Hydrogen Potentials of Mixtures of Acetic Acid and Sodium Acetate." By GEORGE STANLEY WALPOLE. (*Trans.*, 1914, 2501).

The extremely small contact potential between mixtures of acetic acid and sodium acetate and solutions of potassium chloride renders them particularly suitable for electrometric investigation.

Hydrogen potential measurements, corrected for this small potential difference by Bjerrum's extrapolation method, have been made of a series of these mixtures against the N/10-calomel electrode. With these have been compared the calculated results obtained by the well

known energy relationship and Fels' original equation. By the introduction of three rational corrections to this equation, one of them based on the principle of isohydricism, calculated results have been obtained agreeing with those observed to within 1.5 millivolts or less over the whole range from pure acetic acid to a mixture containing thirty-two times as much sodium acetate as acetic acid. The original equation is less accurate than the new equation for solutions containing much sodium acetate, and is inaccurate for mixtures approximating to pure acetic acid in composition. For pure acetic acid Fels' equation is indeterminate, whereas the new equation simplifies to the correct expression for the hydron concentration of acetic acid in terms of its dissociation constant and its concentration.

An electrometric method of standardising sodium acetate capable of development to a high order of accuracy has been devised. Using this method the hydrogen potential of the "standard acetate" solution of Michaelis can certainly be reproduced to within ± 0.10 millivolt, and probably with even a higher order of accuracy.

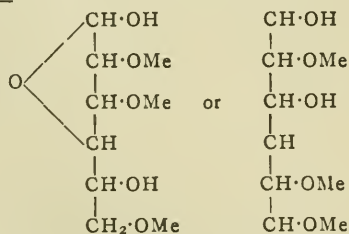
235. "The Effect of Dilution on the Hydrogen Potentials of Acetic Acid and 'Standard Acetate' Solutions." By GEORGE STANLEY WALPOLE. (*Trans.*, 1914, 2521).

The relationship between the hydrogen potential of acetic acid and the logarithm of its dilution is strictly linear. A similar relationship does not hold for "standard acetate."

The electrode potential of moist hydrogen at 760 mm. pressure in "standard acetate" against the N/10-calomel electrode at 18° has been re-determined. The result is 0.6046 volt with saturated potassium chloride solution interposed between the two halves of the cell; corrected for contact potential it is 0.6045 volt. This value agrees to the fourth decimal place with those obtained by Sørensen and by Michaelis.

236. "The Methylation of Cellulose. Part II. Hydrolysis of Methylated Cellulose." By WILLIAM SMITH DENHAM and HILDA WOODHOUSE. (*Trans.*, 1914, 2357).

Further experiments have shown that on the methylation of cellulose by means of sodium hydroxide and methyl sulphate in the manner already described (*Trans.*, 1913, ciii., 1735), the substitution probably does not occur uniformly. This conclusion is supported by a study of the products obtained on hydrolysing the methylated cellulose by means of a very concentrated solution of hydrogen chloride in water. The chief products isolated were monomethyl glucose and dimethyl glucose, both in the amorphous state and probably mixtures of isomeric substances, and a crystalline trimethyl glucose. The monomethyl glucose and dimethyl glucose form osazones. From the fact that the trimethyl glucose does not form an osazone, and from a comparison of its properties with those of trimethyl glucoses of known constitution prepared by Irvine and his collaborators, the formula for the trimethyl glucose derived from methylated cellulose must be either—

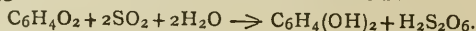


237. "The Reaction of *p*-Benzoquinone with Sulphurous Acid and with Alkali." (Part I.). By JOHN WALLIS DODGSON. (*Trans.*, 1914, 2435).

The usual explanation of the reaction which takes place when *p*-benzoquinone is reduced with sulphurous acid is expressed by the equation—



Sheppard and Mees (*Zeit. Wiss. Photochem.*, 1902, ii., 5) suggested also the formation of dithionic acid:—



The author has found that dithionic acid, if produced at all, is formed in very minute quantities, and that whereas about 80 per cent of *p*-benzoquinone is reduced to quinol with the accompanying oxidation of the sulphurous acid to sulphuric acid, the remainder almost entirely forms quinolsulphonic acid.

The effect of change of temperature on the reactions is inconsiderable, but the presence of much hydrochloric acid almost entirely inhibits both reactions owing to the formation of chloroquinol.

The effect of the addition of alkali is remarkable. In experiments on this point, the *p*-benzoquinone solution was mixed with sulphurous acid to which varying amounts of sodium hydroxide had been added. As long as the amount of alkali used did not exceed that required for the formation of sodium hydrogen sulphite, the result of the reaction, as regards the proportion of sulphate to sulphonate, was practically the same as if sulphurous acid alone had been employed, but the slightest excess caused an immediate and great increase in the amount of sulphonate produced, whilst the yield of sulphate sank to a very small and almost constant quantity.

Further addition of alkali caused a decrease in the amount of sulphonate owing to the action of the alkali on the *p*-benzoquinone.

238. "The Absorption Spectra of the Vapours and Solutions of various Derivatives of Benzaldehyde." By JOHN EDWARD PURVIS. (*Trans.*, 1914, 2482).

The investigation is a continuation of previous work, and the special aim was to see how far and in what directions various isomeric compounds and other compounds derived from benzaldehyde influence the type of absorption when they are in the vaporous condition and in alcoholic solution. The substances examined were:—*o*-, *m*-, and *p*-chlorobenzaldehydes, *o*-, *m*-, and *p*-tolualdehydes, *o*-, *m*-, and *p*-hydroxybenzaldehydes, anisaldehyde, *o*-, *m*-, and *p*-phthalaldehydes, cuminaldehyde, vanillin, benzaldoxime, benzylidene chloride, benzaldehyde sodium hydrogen sulphite, mandelonitrile, benzoyl chloride, and cinnamaldehyde.

239. "The Isomerism of the Oximes. Part V. *m*-Methoxybenzaldoxime, Vanillinoxime, and Veratraldoxime." By OSCAR LISLE BRADY and FREDERICK PERCY DUNN. (*Trans.*, 1914, 2409).

In connection with their work on the underlying causes of the isomerism of the oximes, the authors have investigated three more oximes and some of their derivatives. Whilst there is some evidence that *m*-methoxybenzaldoxime, like anisaldoxime, exists in *anti*- and *syn* forms, vanillinoxime and veratraldoxime show no sign of giving a second isomeride. This is in accordance with the authors' previous experience.

The position of the acetyl group in acetyl-*m*-methoxybenzaldoxime and in monoacetylvanillinoxime has been determined; in each case the oximino- and not the phenolic hydroxy-group is acetylated.

240. "Photokinetics of Sodium Hypochlorite Solutions." (Part II.). By LEO SPENCER. (*Trans.*, 1914, 2565).

The present investigation is a continuation of that of W. C. McC. Lewis (*Trans.*, 1912, ci., 2371) on the decomposition of sodium hypochlorite into sodium chloride and oxygen under the action of the rays from a uviol lamp. A modified form of apparatus has been employed, by means of which it has been possible to keep the temperature of the solution constant to 1°. Velocity-constants have been determined for the full lamp, and for five definite spectral regions extending from λ 578 μ to λ 313 μ . The results obtained bear out Luther's absorption theory of photochemical action. The temperature coefficient of the reaction has been determined, and is shown to be very small. Further, it has been found that the uviol

light slightly accelerates the bleaching action of sodium hypochlorite on linen.

241. "Sodium Amalgams: Specific Volumes and Electrical Conductivities." By ERNEST VANSTONE.

When specific volumes of solid amalgams are plotted against concentrations expressed in percentages by weight, a curve is obtained which shows many discontinuities, indicating the existence of intermetallic compounds.

The agreement with the results of the thermal method is satisfactory. When the specific volumes of liquid amalgams are plotted, a straight line is obtained, showing that intermetallic compounds do not exist in the liquid condition at the temperatures of the experiments, namely, 110°, 184°, and 237°.

The electrical conductivities of liquid amalgams have been determined at 110° and 135°.

The conductivity concentration diagram consists of a smooth curve, thus confirming the results of the experiments on specific volume, that intermetallic compounds do not exist in the liquid condition.

242. "Electromotive Forces in Alcohol. Part V. The Dropping Electrode in Alcoholic Solutions." By EDGAR NEWBERRY. (Trans., 1914, 2553).

The author has carefully examined the behaviour of the dropping electrode in absolute alcoholic solutions, the apparatus devised by Palmaer (Zeit. Elektrochem., 1903, ix., 755) being used with certain modifications which were found necessary. Solutions of sodium chloride containing sodium cyanide, mercuric cyanide, sodium and hydrogen sulphides were used as "null" solutions against the calomel electrode in alcoholic sodium chloride.

Very constant and reproducible results were obtained with various null solutions, but these are shown to be inconsistent with one another and with the theory of the dropping electrode.

243. "Magnesium Boride and Amorphous Boron." By RAMES CHANDRA RAY. (Trans., 1914, 2162).

Amorphous boron was prepared by heating in a current of hydrogen a mixture of magnesium and boron trioxide or fused borax in varying proportions. After freeing the heated mixture from the admixed impurities, and after washing the residue and drying it in a vacuum, a greyish red powder was obtained. This so-called amorphous boron was always found to contain much oxygen, thus confirming Weintraub's experiments. Probably the so-called amorphous boron is a solution in elementary boron, of a lower oxide of boron and of magnesium oxide, possibly in combination as a borite. Boron could be obtained in a state approaching purity in only one form, namely, that of a crystalline substance which is practically insoluble in nitric acid.

On heating crystalline boron with magnesium, no reaction took place. When a mixture of 1 part of boron trioxide with 2½ parts of magnesium powder was heated to a red heat in a current of hydrogen for forty-five minutes, a mixture of magnesium boride (Mg₃B₂) and oxide in the theoretical proportions was obtained. A similar mixture was also obtained on heating the so-called amorphous boron with magnesium. From the results of analyses it was proved that at a red heat and under normal pressure only one boride, having the formula Mg₃B₂, is formed. On heating the boride magnesium was driven off, and the greater part of the boron separated in the crystalline form.

244. "Diphenyl-2:3:2':3'- and 3:4:3':4'-Tetracarboxylic Acids." By JAMES KENNER and ANNIE MOORE MATHEWS. (Trans., 1914, 2471).

An account having been given of the preparation and reactions of diphenyl-2:3:2':3'-tetracarboxylic acid, it is suggested that the results favour the usual formula for diphenyl rather than that proposed by Kaufler. Additional evidence is also adduced in favour of the explanation previously advanced of the ready formation of dibenzocycloheptadiene derivatives from those of 2:2'-dimethyl-di-

phenyl (Kenner and Turner, Trans., 1911. xcix., 2101; Kenner, Trans., 1913. ciii., 615).

Tetramethyl diphenyl 3:4:3':4'-tetracarboxylate was prepared from dimethyl 4-iodophthalate, and its properties, as well as those of the tetracarboxylic acid, are shown to agree in the main with those of a diphenyltetracarboxylic acid prepared by Liebermann (Ber., 1912. xlv., 1187). The constitution of the latter compound was therefore decided.

245. "The Composition of Coal." (Part II.). By DAVID TREVOR JONES and RICHARD VERNON WHEELER. (Trans., 1914, 2562).

The results of distilling bituminous coal in a vacuum at 350° are described. It is shown that the liquid distillates are similar in character and composition to those obtained from the same coal at 430° (Trans., 1914. cv., 140).

The presence in the oils obtained at 350° of aromatic compounds, previously assumed to arise from the decomposition, with elimination of hydrogen, of hydrogenated aromatic nuclei at temperatures not much below 400° (the temperature at which dihydronaphthalene had been found to decompose), is explained by assuming a decomposition analogous to that observed by Cannizzaro (Gazzetta, 1884, xiii., 385) in the case of santonous acid which, between 300° and 350°, yields chiefly 1:4-dimethyl-5:8-dihydro-β-naphthol and propionic acid, hydrogen not necessarily being eliminated.

246. "Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part IX. The Rotatory Powers of 1-Naphthyl-n-hexylcarbinol and its Esters." By JOSEPH KENYON and ROBERT HOWSON PICKARD.

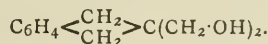
dl-1-Naphthyl-n-hexylcarbinol melts at 41°, and its hydrogen phthalate at 102—104°. The latter is readily resolved into its optical isomerides by fractional crystallisation of the brucine salt from acetone. The d-carbinol melts at 41°, and in the supercooled state is laevorotatory, exhibiting "anomalous" dispersion. It has a complex dispersive power at temperatures below 180°, but above this temperature the observed optical rotations obey the law of simple dispersion. Ten esters (ranging from the acetate to the n-undecate) of the d-carbinol, and also the acetate of l-1-naphthylmethylcarbinol have been prepared, and all possess complex dispersive power (at least) up to a temperature of about 200°.

247. "The Atomic Weight of Mercury." By HERBERT BRERETON BAKER and WALTER HENRY WATSON. (Trans., 1914, 2520).

Mercury was converted into mercuric bromide by direct treatment with liquid bromine, excess of the latter being removed by heating to 70—80° in a current of dry air. A trace of adsorbed bromine still remaining in the weighed product was expelled by fusion, and determined by passing it into a solution of potassium iodide and titrating with N/10 thiosulphate. In nine completed experiments values ranging from 200.50 to 200.62 were obtained for the atomic weight of mercury, the mean result being:—Hg = 200.57 ± 0.008.

248. "The Reduction Products of Ethyl Hydrindene-2:2-dicarboxylate." By JAMES KENNER.

Bouveault and Blanc's method of reduction was applied to the above ester with the object of preparing ωω'-dihydroxy-2:2-dimethylhydrindene,—



This compound (m. p. 112.5°) was, however, only produced to the extent of 3 per cent of the calculated amount, the main product being 2-hydroxymethylhydrindene,

$\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array} > \text{CH}\cdot\text{CH}_2\cdot\text{OH}$ (m. p. 33°), 2-bromomethylhydrindene, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array} > \text{CH}\cdot\text{CH}_2\text{Br}$ (m. p. 21°), reacted only slowly with ethyl malonate and with potassium phthalimide.

These results are discussed in connection with the general problem of the stability of compounds containing a quaternary carbon atom, and the attempt is made to supply a theoretical basis for this subject.

249. "Solutions of Bromine in Water, Nitrobenzene, and Carbon Tetrachloride." By ALFRED FRANCIS JOSEPH.

Determinations have been made of the colour and solution-volume of bromine in the above three solvents. In carbon tetrachloride bromine appears to have the same colour as when in a state of vapour at the same concentration; in nitrobenzene the colour is only about two-thirds, and in water about one-third as intense. The solution-volume (from low concentrations up to 60 grms. per litre) increases in each case to a maximum, which is greatest for carbon tetrachloride and least for water.

Bromine mixes freely with nitrobenzene and carbon tetrachloride; the rate of its removal in a current of air is twice as fast from solution in the latter as in the former.

250. "Volatile Oil from the Leaves of *Barosma venusta*." By ERNEST GOULDING and OSWALD DIGBY ROBERTS.

The leaves of *Barosma venusta*, Eckl. and Zeyh., yield about 2 per cent of a volatile oil, which has a lemon-yellow colour, a pleasant odour, $D_{15/15}$ 0.865, and n_D^{22} 1.471. The percentage composition of the oil is approximately as follows:—Hydrocarbons, chiefly or entirely myrcene, 43; aldehydes, chiefly or entirely anisaldehyde, 0.5; phenols, 0.2; methylchavicol, 21.4; alcohols, partly linalool (calculated as $C_{10}H_{17}OH$), 14.3; esters (calculated as $C_{10}H_{17}OAc$), 2.2; sesquiterpenes, &c., 18.4.

251. "The Limits of Inflammability of Mixtures of Methane and Air." By MAURICE JOHN BURGESS and RICHARD VERNON WHEELER.

The different limits of inflammability of mixtures of methane and air, dependent on the direction in which the flame has to travel, are recorded. The results are as follow:—

	Methane, per cent.	
	Lower limit.	Higher limit.
Central ignition in large globe	5.6	14.8
Vertical tube closed at both ends—		
(a) Ignition at bottom	Not less than 5.4	Not more than 14.8
(b) Ignition at top ..	6.0	13.4
Horizontal tube closed at both ends—		
Ignition at one end ..	$\left. \begin{array}{l} 5.4 \text{ (flame travels only along top of tube)} \\ 5.6 \text{ (methane all burnt)} \end{array} \right\} 14.3$	

252. "The Propagation of Flame in "Limit" Mixtures of Methane, Oxygen, and Nitrogen." By MAURICE JOHN BURGESS and RICHARD VERNON WHEELER.

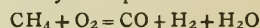
A series of determinations was made of the amounts of methane required to form higher- and lower-limit mixtures with various "atmospheres" ranging between air and a mixture of air and nitrogen containing 13.45 per cent of oxygen. The results were as follows:—

Atmosphere.		Methane, per cent.	
Oxygen.	Nitrogen.	Lower limit.	Higher limit.
20.90	79.10 (air)	5.60	14.82
19.22	80.78	—	12.93
18.30	81.70	—	11.91
17.00	83.00	5.80	10.55
15.82	84.18	5.83	8.96
14.86	85.14	6.15	8.36
13.90	86.10	6.35	7.26
13.45	86.55	6.50	6.70
13.25	86.75	No mixture capable of propagating flame.	

An attempt was made to calculate the heat balances during the spread of flame in these limit mixtures from the general equation:—

$$(c'M + c''P)(T' - t) + q = xQ \dots (1).$$

It was shown that when methane is the combustible gas the calculations are complicated by the fact that combustion in the flame is incomplete. It was therefore necessary to obtain samples of the "flame gases" while the flames were travelling through the mixtures. Analyses of these gases showed a regular relationship between the ratios O_2/CH_4 in the original mixtures and the proportions of methane that burned completely to form carbon dioxide and steam. The opinion is advanced that the essential reaction in the propagation of flame in the limit mixtures is that represented by the equation—



The general equation (1) was modified in accordance with this view, and the heat balances for all the limit mixtures calculated. It was found that Q , the heat evolved, and q , the heat unaccounted for or "lost," were practically proportional to one another, the heat unaccounted for averaging for each mixture 35 per cent of the total evolved. The question of the variation with temperature of the heat transmitted from flames by conduction, convection, and radiation is discussed.

Attention is drawn to the preferential burning of hydrogen over carbon monoxide in the flame gases of al. mixtures of which the ratio O_2/CH_4 was greater than 1.51

253. "The Propagation of Flame in Mixtures of Methane and Air. The Uniform Movement." By RICHARD VERNON WHEELER.

Mallard and Le Chatelier's determinations of the speed of travel of flame during the "uniform movement" in methane-air mixtures (*Ann. des Mines*, 1883, [viii.], iv., 324) were repeated.

It was shown that their results were incorrect, mainly because the methane they used, prepared from sodium acetate, was very impure.

The curve obtained on plotting speeds as ordinates and percentages of methane as abscissæ showed that there was practically no difference between the speeds attained in mixtures containing from 9.4 to 10.5 per cent of methane. On either side of these percentages the speeds diminished fairly regularly; but near the lower- and higher-limits of inflammability the curve flattened more noticeably towards the higher-limit, becoming, ultimately, nearly horizontal.

The speed of travel of flame was found to be uniform throughout in the lower- and higher-limit mixtures, which contain (horizontal propagation of flame) 5.4 and 14.3 per cent of methane respectively, and to be the same for both.

(To be continued.)

MEETINGS FOR THE WEEK.

MONDAY, 14th.—Royal Society of Arts, 8. (Cantor Lecture). "The History and Practice of the Art of Printing," by R. A. Peddie.

WEDNESDAY, 16th.—Royal Society of Arts, 8. "Testing Pigments for Permanence of Colour," by Sir William de W. Abney, K.C.B., F.R.S.
Microscopical, 8. "X-rays in Relation to Microscopy," by J. E. Barnard.

THURSDAY, 17th.—Royal Society of Arts, 4.30. "The Indian Indigo Industry," by F. Mollwo Perkin.

Chemical, 8.30. "Isodibenzoylglucosylase," by F. Tutin. "Platini-, Mercuri-, and Cuprichloro-mercaptides and Tautomerisation of Organic Thiobodies as brought about through the Agency of Mercuric, Cupric, and Platonic Chlorides," by P. C. Ray.

FRIDAY, 18th.—Physical, 5. Exhibition and Description of some Apparatus for Class Work in Practical Physics, by G. F. C. Searle. "A Vacuum Guard Ring and its application to the Determination of the Thermal Conductivity of Mercury," by H. R. Nettleton.

THE CHEMICAL NEWS

VOL. CX., No. 2873.

THE SUPPLY OF CHEMICALS TO BRITAIN AND HER DEPENDENCIES.*

By Sir WILLIAM A. TILDEN, D.Sc., LL.D., F.R.S

To those who can look back over half a century, the progress of scientific and industrial chemistry, and the relations of the one to the other, present many features of extreme interest. After the days of Lavoisier, and during the earlier part of the nineteenth century, the foundations of theoretical chemistry were laid by the efforts, contemporaneous but independent, of the chemists of England, France, and Sweden. The great names associated with the movement include Davy, Faraday, Dalton, Gay-Lussac, Dumas, and Berzelius. There were no German chemists of the first rank in those days, and if we look among them for fundamental discoveries we can only find one of considerable importance, namely, the discovery of isomorphism by Eilhard Mitscherlich in 1819. But the birth of Justus Liebig at Darmstadt, in 1803, gave to German science a leader whose influence stretches down to our own day, and is felt wherever chemistry is studied or practised. The department of organic chemistry has been the field in which the most remarkable successes have been won, though not wholly as sometimes represented, by the German chemist.

The relation of optical activity to atomic constitution was the discovery of Le Bel, a Frenchman, almost simultaneously with van't Hoff, a Dutchman, and the application of their theories to the phenomena presented by compounds other than those of carbon, was illustrated in the first instance by Smiles, and by Pope and Peachey, all of whom are Englishmen. It will also be only fair to state that while we readily acknowledge with admiration the brilliant work of Von Baeyer and Emil Fischer in connection with the synthesis of indigo, the sugars and the proteins, the fundamental principles which underlie all chemical theory, have been established almost entirely by the chemists of other nations. It is only necessary to recall such subjects as the atomic theory, the periodic law, Faraday's laws of electrolysis, the theory of free ions, the phenomena of radio-activity, and the discovery of radium, to show that in laying down broad general principles German chemists have not usually been the first in the field, though at later stages they have shown great and commendable activity.

Turning now to the position of industrial chemistry, a single brief quotation from the "Report on Chemical and Pharmaceutical Products and Processes" in the International Exhibition of 1862, from the pen of A. W. Hofmann, then Professor of Chemistry in the Royal College of Chemistry and Royal School of Mines, London, will be sufficient. He says (p. 3):—"The contributions of the United Kingdom, and in particular the splendid chemical display in the Eastern Annexe, prove the British not only to have maintained their pre-eminence among the chemical manufacturers of the world, but to have outdone their own admitted superiority on the corresponding occasion of 1851."

On referring to the table of statistics which appears on the same page of the report, we find that of the 762 exhibitors in the class, the United Kingdom was represented by 200, while Germany, Austria, the Zollverein, and the Hanse towns together mustered only 136. France stood next with 115 exhibitors. It will be remembered that at the date of the exhibition, the discovery of the so-called aniline colours was bearing very important industrial

fruit. Mauve, or aniline purple, was discovered by W. H. Perkin in 1856, and aniline red was first obtained industrially by Verguin and Renard frères of Lyons a few years later.

It is also interesting to notice that among the early investigators and patentees of processes connected with the production of colour from coal-tar hydrocarbons, only English and French names are to be found, with the significant exceptions of Hofmann and Caro, both of whom were at that period resident in England. At this time synthetic chemistry in the modern sense was as yet unpractised because unknown. Such an important substance as salicylic acid, for example, was a mere laboratory product, obtainable only from natural sources.

But the activity of the chemical industries in the United Kingdom is not to be measured only by reference to subjects such as those of the coal-tar colours, nor by the number of exhibitors in an international exhibition even at that early period in the history of exhibitions, at which manufacturers were far more eager to find a place than they have been in more recent times. Statistics in relation to the development of the alkali trade show how rapidly the production of what are called "heavy chemicals" was proceeding at this period. Figures derived from returns collected by Mr. Christian Althusen from 81 per cent of the manufacturers in the United Kingdom, immediately after the first Great Exhibition, are shown below. These may be compared with statistics prepared by Mr. W. Gossage for the year 1861 immediately before the Exhibition of 1862 (Gossage's "History of the Soda Manufacture") :—

	1852. Tons.	1861. Tons.
Soda ash	71,193	156,000
Soda crystals ..	61,044	104,000
Bicarbonate .. .	5,762	13,000
Bleaching powder..	13,100	20,000

The value of these products for 1852 was estimated at about 1½ million pounds, while the value of the products of 1861 was calculated by Mr. Gossage at upwards of two millions sterling.

The Board of Trade has recently issued a Bulletin concerning German competition in the United Kingdom market, and on page 2 we find the statement that the soda compounds, excluding chromates and bleaching powder, produced in the United Kingdom in the year 1907, are valued at £3,390,000. The imports from Germany in 1912 are valued at only £8700. As to bleaching materials, the product of the United Kingdom for 1907 is estimated at £527,000, while the import from Germany for 1912 was £44,600.

From these figures the easy deduction is made that "the imports of these chemicals into the United Kingdom from Germany are relatively insignificant when compared with the output of the same articles in this country. It is clear that in these particular lines British manufacturers have no need to fear German competition in the home market."

Similar remarks apply to aluminous compounds, coal-tar products not dyes, the cyanides, sulphuric acid, and other acids for which the Bulletin may be consulted. It thus appears that the British manufacturers of sulphuric acid and soda, from the early times of a century ago, have been able, up to the present, to hold their own against foreign competition, and have thus added substantially to the revenues and well-being of their country.

The immense advances in every direction made in all civilised countries have brought demands in steadily increasing quantities for a variety of materials of which many were unknown to the generations immediately preceding our own. These are almost all the outcome of the progress in our own time of chemical knowledge. Since the introduction of the coal-tar dyes the development of chemical theory has rendered possible the production in the laboratory of a large number of organic substances which are either identical with compounds already known as occurring in Nature, or from

* Read before the Royal Society of Arts, November 25, 1914.

their ascertained physiological action have added incalculably to the resources of the physician and surgeon in relieving pain and in curing disease. These include not only drugs for internal administration, but antiseptics, the use of which was only beginning to be recognised at the time of the Exhibition in 1862 (Hofmann's "Report," pp. 104—105).

To these must be added essential oils and other volatile aromatic substances, the application of which to perfumery and flavouring has undergone a stupendous development during the last thirty years.

The innumerable applications of photography have also led to a demand for developing, fixing, and toning materials, as well as for plates and films on a very large scale.

The arts of peace as well as the operations of war have also led to the production of explosives of many new types formerly unknown.

There is also another department of business which requires notice, and that is the demand for pure chemical reagents for analysis and research which has increased to an extent very difficult to calculate, but is manifestly very large. The modern university and technical colleges, nearly the whole of which have come into existence within the last forty years, the large body of public analysts appointed under the Sale of Food and Drugs Act, 1875, the establishment in nearly all the public schools and high schools of laboratories for teaching chemistry, as well as the numerous technical laboratories connected with such institutions as the Government Laboratory, the National Physical Laboratory, the Metropolitan Water Board, and many others, afford sufficient evidence that there are several hundreds of chemical laboratories distributed over the United Kingdom in which pure chemicals are required for analytical purposes.

Now leaving to the department of "heavy chemicals" all such things as agricultural and horticultural washes, coarse disinfectants, and artificial manures, the question arises, How do we in England stand in regard to the supply of drugs, dyes, photographic chemicals, and perfumes at a time when many of these things are very urgently needed?

It may be safely asserted that the sources of supply of all these materials in the United Kingdom are seriously inadequate. And, further, we may point to the acknowledged fact that many of the dyes, nearly all the synthetic drugs and photographic materials have been systematically imported from Germany.

The Annual Statement of the Board of Trade (p. 108) shows that in 1913 we imported from Germany:—

Alizarin and anthracene dyes	271,119
Aniline and naphthalene dyes	1,382,478
Synthetic indigo	76,681

£1,730,278

Under the head of "Drugs, unenumerated, including Medicinal Preparations" (p. 107), out of a total of imports from foreign countries and from British possessions amounting to £1,302,860, more than one-fourth, or to the value of £332,464, was in 1913 received from Germany. From this is to be deducted the inconsiderable amount of dyes and other chemicals from coal-tar, valued at £24,691, exported in 1913 to Germany (p. 300). According to the Final Report on the First Census of Production of the United Kingdom for 1907 (p. 547), this country made 139,000 cwt. of coal-tar dyes, valued at £373,000, of which practically the whole was consumed at home.

As to fine chemicals for analysis and for research, there are no figures available, but it may safely be said that there has been no appreciable production of these things in this country. If such a statement is met by protests from manufacturers who profess to supply these materials it is only necessary to refer to the experience of analysts and directors of research laboratories, which has compelled many of them to resort habitually to German makers for their supplies of trustworthy reagents.

It we are ever to be in a position to supply ourselves and our Dependencies with the dyes, the drugs, and the rest of the fine chemicals required in our work, it will only be achieved after a careful review of the circumstances which led to the removal of the industries from this the country in which many of them originated, together with a determination to take to heart the lessons of the past.

A chemical manufacturer, discussing the neglect of fine chemicals in this country, recently made the remark:—"What does it matter if we are making money?" I venture to say that that view expresses neither patriotism nor common sense. For the same principles which have served as the basis of the German success in relation to dyes and fine chemicals apply equally to the production of heavy chemicals, and already German chemists have been boasting that, having secured the trade in the former, they are about to attack the latter.

The export trade in sulphuric acid alone is already three times as great from Germany (1912) as from the United Kingdom (1913), as shown by the figures given in the recent Bulletin issued by the Board of Trade (Commercial Intelligence Branch, October, 1914).

The recent success of Professor Haber, of Karlsruhe, in the synthetical production of ammonia from hydrogen and atmospheric nitrogen, a process which has been put into operation on an industrial scale by the Badische Company, ought surely to carry something significant to the unprejudiced mind. Neither is it superfluous to point to the extensions taking place in several countries of operations in which the nitrogen of the atmosphere is being fixed in the form of cyanamide, of nitrites and nitrates, in which the industrial lead has been taken by Germany, which also supplies a large proportion of the capital, though at present not to the exclusion of the British.

The extent to which the German chemist arrogates to himself the whole field of scientific and industrial chemistry, is illustrated in the report (given in full in *Nature*, lxxxv., p. 558) of a lecture given by Professor Emil Fischer on January 11, 1911, in the presence of the Emperor, on the occasion of the inauguration of the Kaiser Wilhelm Gesellschaft zur Förderung der Wissenschaften. It is at least unpleasant to hear of a man so eminent as Professor Fischer, and so worthy of respect, treating the subjects of his discourse as though every one of them had originated and been developed in Germany. Perkin is indeed referred to as the discoverer of mauve, but every other foreign name is omitted.

If I now try to recall some of the circumstances which led to the gradual transference of the colour industry from this country to Germany, and the failure to establish here any appreciable production of the synthetic drugs and other chemicals now so urgently needed, it will not be the first time the facts have been stated and the obvious conclusions deduced therefrom.

All the substances referred to belong to the department of organic chemistry, and it might perhaps be supposed that neglect of this branch of the science by the chemists of this country was the cause of the loss of business. When Hofmann was unfortunately allowed to leave the College of Chemistry to return to his own country a check was for some time observable in the output of research among us, but it must be remembered that the number of institutions in all countries in which the study of chemistry was pursued was then relatively small. Even in Germany the Chemical Society in Berlin did not come into existence till 1867, and up to that time there had been no laboratory for practical instruction in chemistry in the university of that city.

For the last thirty years, however, the progress of research in this country has gone forward at an increasing rate, though still less rapidly than in Germany. The slow development of chemical teaching and research in this country was attributed by many people to the anti-scientific influences at work in our universities, and especially the older universities. This point of view was exposed very clearly and forcibly by the late Sir William

Perkin in presidential addresses delivered to the Chemical Society and the Society of Chemical Industry in 1885. And up to this time it would be indeed difficult to exonerate Oxford and Cambridge from responsibility in the evil example shown by those great seats of learning. But since that day many changes have taken place, and great advances have been made. What is wanted in the British universities is, first of all, that no man shall in future be appointed to a professorship, or indeed to any teaching post in connection with physical or natural science, who does not show his ability to instruct in the higher branches of his subject by the character of the researches which he continues to carry out during his tenure of office; and, secondly, such a change in the curriculum and endowments that there may be not only a supply of instruments and materials but a sufficient body of trained assistants in the form of advanced students to enable the professor to pursue without delay any promising line of investigation.

Notwithstanding the difficulties which stand in the way the scientific chemists of this country are, however, not idle. Evidence of this may be seen in the *Transactions* of the Chemical Society, the volume of which for 1913 contains 238 papers extending over more than 2300 pages. And when it is remembered that these papers have survived the severe censorship exercised by the Publication Committee of the Society the result must be considered encouraging. It appears, then, that it is not to the scientific part of the chemical world that blame attaches in recent times.

Forty years ago it would be safe to say that there were practically no chemists engaged in the direction of the chemical works of this country, and by chemists I mean fully qualified scientific men. Probably in the palmy days of colour making it would have been difficult to meet with a British manufacturer who had ever heard of Kekulé's benzene theory, or would have thought it worthy of a moment's notice by a practical man. And yet at the Kekulé jubilee in 1890 a representative of the German coal-tar colour industry declared that the prosperity of Germany in this direction was primarily due to this theoretical conception. Even in much later times the chemical manufacturer in this country has repeatedly had facts laid before him which ought to have attracted his serious attention. One of the most convincing statements was laid before this Society by Professor Meldola on May 13, 1886, and one would suppose that the figures then given would have been sufficient to create well-founded alarm. For he showed, on the testimony of a considerable number of prominent English dyers, that already about nine-tenths of the colours employed by them were imported from Germany. Again, in a lecture given before the British Association in 1901, on the "Relative Progress of the Coal Tar Industry in England and Germany during the past fifteen years" (*Journal of the Society of Dyers and Colourists*, for December, 1901), Professor Green showed clearly the steady increase in the imports of dyestuffs from Germany into England, and the steady decline in the production of similar materials in England.

Finally, we have the fact known to all the world that one of the most notable triumphs of German chemical industry is the production of synthetic indigo made from naphthalene on a scale so large as to have almost driven the Indian planter from the field. In this case we have over again a story nearly corresponding to the history of the introduction of artificial alizarin in 1869, an event which was speedily followed by the abandonment of the cultivation of madder in the south of France and elsewhere. And to-day we learn from the Board of Trade statement for 1913 that we imported indigo from Germany to the value of £76,681, while the value of the natural indigo from India has declined from £124,112, in 1909, to £48,208 in 1913. As to the cause of this serious reduction of chemical business authorities are unanimous.

Perkin in the address to the Chemical Society already quoted, attributed the success of the German industries to

the employment of high-class chemists (*Trans. Chem. Soc.*, xlv., [1884], p. 219 *et seq.*).

The same view was expressed by Professor Meldola in his paper before this Society in 1886. "The strength of our competitors," he says, "is in their laboratories and not, as here, on the exchanges."

Professor Green stated as his opinion, in the lecture referred to, that the remedy for the present state of affairs can only be found in a better appreciation of the value of science throughout the length and breadth of the land, and that it is not so much the education of our chemists which is at fault as the scientific education of the public as a whole. Nor can much improvement be expected till the public, including manufacturers, can be disabused of the fallacy that a year or two of technical training pumped into an ignorant schoolboy will produce a better works chemist than a university course of scientific study laid upon the foundation of a good general education.

If these are supposed to be merely the prejudiced opinions of British chemists the sentiments expressed by German manufacturers themselves may be appealed to.

(To be continued).

(A). THE HARDNESS OF SOLID SOLUTIONS.*

By Dr. CECIL H. DESCH, Glasgow.

Most of the recent contributions to the subject of the hardness of metals have dealt with the hardening produced by quenching, by cold-working, or by surface flow. A complete theory of hardening must, however, also take into account the facts relating to the hardness of solid solutions (mixed crystals). It is well known that the hardness of the alloys of a pair of completely isomorphous metals, such as gold and silver, is not an additive property, but is always greater than the hardness calculated by the rule of mixtures. For example, in the instance just mentioned an alloy containing equal weights of gold and silver is about twice as hard as either of the component metals, and alloys of gold and copper, or of copper and nickel, present similar maxima in the curve of hardness. When the two metals form a compound which enters into solid solution with both of its components, the curve of hardness presents a downward-directed cusp at the composition of the compound, with a maximum on each side. This case is very clearly exemplified by the remarkable alloys of cadmium and magnesium, the cusp corresponding with the compound $MgCd$ (G. G. Urazoff, *Zeit. Anorg. Chem.*, 1911, lxxiii., 31). The same conditions may be traced, although complicated by other factors, in the alloys of copper with zinc and tin, and of silver with magnesium.

The hardness of the elements is a periodic function or the atomic weight, the curve of hardness bearing a close resemblance to the curve of atomic volume. Benedicks found that the hardness is closely proportional to the atomic concentration, that is, the number of atoms in unit volume, expressed by the quotient of the density by the atomic weight, and the rule has been extended to compounds by employing the mean atomic weight (molecular weight divided by the number of atoms in the molecule). A very close agreement is not to be expected, in view of the numerous sources of error in determining the relative hardness of different solids. It has been shown that the most considerable deviations are found in substances which exhibit very perfect cleavage, and therefore yield to an abnormal extent when submitted to the usual methods of testing (J. L. C. Schroeder v. d. Kolle, *Proc. k. Akad. Wetensch. Amsterdam*, 1901, iii., 655).

A closer agreement between theoretical and experimental values for the hardness has been obtained by the

* Contribution to the General Discussion on "The Hardening of Metals," held before the Faraday Society, Nov. 23, 1914.

application of Van der Waals' equation to solids (T. Traube, *Ber.*, 1909, xlii., 1594; *Zeit. Anorg. Chem.*, 1903, xxxiv., 413; 1904, xl., 372; C. Benedicks, *Ibid.*, 1905, xlvii., 455; see also G. Tammann, "Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen," Leipzig, 1907, p. 31). In the equation—

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

$\frac{a}{v^2}$ is termed the internal pressure, and an arrangement of the elements in order of their internal pressure coincides almost completely with the order of hardness. This is illustrated by the following figures, extracted from a table given by Traube, to which the values of the atomic concentration have been added:—

Element.	Atomic concentration.	Internal pressure (megabars).
Potassium	0.022	8,190
Sodium	0.042	18,500
Lead	0.055	51,500
Tin	0.061	68,700
Copper	0.140	236,100
Nickel	0.151	306,300
Carbon (diamond)	0.290	5,458,000

On both of these views, the increased hardness of solid solutions is due to an increase of pressure, regarded by Benedicks as osmotic pressure and by Traube as internal pressure in the above sense. Benedicks has calculated the osmotic pressure due to dissolved carbide in a quenched steel containing 0.89 per cent of carbon to be 137.8 atmospheres, assuming the carbide molecule to be Fe_3C , or 68.9 atmospheres, assuming it to be Fe_6C_2 .

These relations make it clear that the problem of hardness is connected with that of the close packing of the atoms or molecules in a solid. Different views have been taken as to the nature of the packing in the metals. According to Barlow and Pope (*Trans. Chem. Soc.*, 1907, xci., 1150) those metals which crystallise in the regular system are represented by the cubic closest-packed assemblage of equal spheres. "It must not, however, be concluded that for this reason all the spheres composing the structure are identically treated in the packed assemblage; some, selected homogeneously, might be differently treated from others and the assemblage yet exhibit holohedral, hemihedral, or tetrahedral symmetry of the cubic system according to the particular type of homogeneous distribution of the preferentially treated spheres."

In the simplest cubic arrangement, each sphere is in contact with twelve others, and compression continued until the intervening spaces are completely obliterated converts each sphere into a regular rhombic dodecahedron. On the other hand, Solas assumes comparatively loose packing of the component spheres (*Proc. Roy. Soc.*, 1898, lxi., 270; 1908, A, lxxx., 267).

It has recently been found possible to apply an experimental test. The discovery that the reflection of X-rays by crystals bears an intimate relation to the internal structure of the crystal provides a means of investigating this structure. So far only one metal has been examined in this way. Crystals of native copper, when submitted to the action of X-rays, reflect the latter at certain angles, indicating that the unit of the space-lattice for this metal is the face-centred cube (W. L. Bragg, *Phil. Mag.*, 1914 [vi.], xxviii., 355). This structure corresponds with the simplest closest-packed cubic arrangement, in which every atom, regarded as a sphere or parallelohedron, is in contact with twelve similar spheres or parallelohedra. Whether closest-packing is absolutely essential to the interpretation of the experimental results is, however, not quite clear, and the opinion of an expert crystallographer on this point would be of interest.

There are many types of crystalline solid solution, and it will be advisable to consider only the simplest of these at present. The most important pairs of metals which form

complete series of solid solutions with one another are: gold-silver, gold-copper, copper-manganese, copper-nickel, gold-platinum, platinum-iridium, and antimony-bismuth. All but the last of these pairs crystallise in the cubic system. The pair magnesium-cadmium may be omitted on account of the complication introduced by the compound MgCd . This leaves six pairs which are fairly well known, and of which the members crystallise in similar simple forms. In each case, the two components have nearly equal atomic volumes; and these volumes are small, gold, silver, copper, manganese, nickel, and the platinum metals all occurring at or near the minima on the periodic curve of atomic volumes. The following values may be adopted:—

Au	10.202	Ni	6.64
Ag	10.233	Pt	9.06
Cu	7.077	Ir	8.61
Mn	7.44		

The case of the alloys of gold and silver may be regarded as typical. The atomic volumes of the two metals are very closely similar. The internal crystalline arrangement of silver and gold has not yet been determined by the method employed for copper, but the external crystallographic characters are almost identical, and it is probable that an exactly similar space-lattice will be found to fulfil the conditions of all three metals. The difference between the atoms of gold and silver is then so small that the two space-lattices should interpenetrate freely without appreciable distortion, and the solid solutions of the two metals should be crystallographically indistinguishable from their components. The available data are too scanty to decide whether this is actually the case. The native alloy, electrum, is described as similar. It is hoped that an examination of the alloys by the X-ray method may shortly be undertaken. The fact that the freezing-point and solidus curves of the gold-silver system approach so closely to a straight line also suggests that the mixture is of a very simple type, whilst the specific volume is strictly proportional to the concentration, the greatest deviation from the mixture rule being only + 0.2 per cent. Diffusion of silver into gold takes place very readily; for example, a gold wire, 0.46 mm. in diameter, was coated electrolytically with silver until the compound wire contained 62.7 per cent Ag. The electrical conductivity was determined, and the wire was then heated at 900°. The conductivity gradually fell, and reached a final value after 120 hours. The diameter of the wire was then 0.98 mm., and its conductivity was that of a homogeneous alloy of the same dimensions and composition (G. Bruni and D. Meneghini, *International Journal of Metallography*, 1912, ii., 26).

These facts indicate that the solid solutions of gold and silver are of a very simple character. Nevertheless, the hardness of the alloys is considerable, attaining a maximum value which is twice that of the pure metals, whilst the electrical conductivity is correspondingly diminished, passing through a minimum. Of the two explanations which first suggest themselves, an alteration in the closeness of packing seems improbable in view of the equality of the atomic volumes throughout the alloys. There remains the assumption of a condition of internal strain. On this view, the hardness of a solid solution is due to the same cause as that of a cold-worked metal, namely a disturbance of the crystalline structure, giving rise to an amorphous or irregular arrangement of the atoms or molecules, or at least, if the conditions be regarded from a kinetic point of view, to a constraint of the atomic or molecular motions. This is an aspect of the problem which has been treated by Dr. Beilby, but has received very little attention from other writers.

According to Tammann (*Lehrbuch der Metallographie*, Leipzig, 1914, p. 332), the increased hardness of solid solutions is due to the fact that "the attractive force between two different molecules is always greater than the attractive force between two similar molecules in

the same mixture." It is therefore to be expected that the attraction, and consequently the hardness, should be a maximum in the solid solution containing equal molecular proportions of the two components, and this rule is approximately fulfilled in the case of several of the series investigated by Kurnakoff and Schemschuschny (*Zeit. Anorg. Chem.*, 1908, ix., 1). It may be noted that the rule is confirmed by application to cases in which an inter-metallic compound is formed. Thus, the compound MgCd forms a continuous series of solid solutions with both of its components. The maximum hardness is not that of the compound, although this is harder than either component, but the curve plotted with atomic percentages presents two maxima, approximately midway between Mg and MgCd and between MgCd and Cd respectively. These are the two compositions at which there is the greatest admixture of foreign molecules.

Direct evidence of a constrained condition of the molecules of a solid solution, or of a disturbance of the internal crystalline structure, is not easy to obtain in the case of metals, but the conditions are more favourable in that of isomorphous salts. These salts frequently exhibit "optical anomalies," indicating the presence of internal strain, and such a condition is often assumed to be usual. It is, however, by no means necessarily the case. In his very careful work on isomorphism, Retgers (*Zeit. Physikal. Chem.*, 1889, iii., 497) has shown that the anomalies do not always occur, and has used their absence as one of the tests of the homogeneity of isomorphous "mixed crystals" required for investigations of density. The most conspicuous examples of crystals exhibiting optical anomalies are those of salts crystallising from solutions containing dyes. Here there is no question of the interpenetration of space-lattices, and the production of a strain in the crystals is readily comprehensible, but where two salts of almost identical molecular volume are concerned, it seems probable that Retgers' view is correct, and that optical anomalies are absent when sufficient care is taken to conduct the crystallisation slowly and in presence of a large excess of the saturated solution.

It is usually stated, also, that solid solutions crystallise less readily, or yield less perfect crystals, than pure substances. This is not invariably the case, but the fact has been observed so frequently that it must be regarded as evidence for a certain disturbance of crystalline structure in solid solutions.

The heat of formation of solid solutions has hitherto been determined only in the case of isomorphous salts, and then by an indirect method, the heat of solution of the solid solution in water being compared with that of a mechanical mixture of the components in the same proportions. The pairs of salts which have been examined satisfactorily by this method—NaCl—KCl, NaBr—KBr, NaI—KI, KCl—RbCl, KCl—KBr, KBr—KI, KCl—KI, NaNO₂—NaNO₃—all give results indicating a negative heat of formation for the solid solution (G. Bruni, *Mem. R. Accad. Lincei*, 1912, p. 50). For two of these pairs, namely, KCl—KBr and KBr—KI, the hardness curve, as determined by measuring the pressure required to produce flow through an orifice, passes through a maximum not far from the middle of the series (T. B. Vrschesnevsky, *Fourn. Russ. Phys. Chem. Soc.*, 1911, xliii., 1364).

It will be seen that the data which are available for drawing a conclusion as to the hardness of solid solutions, even in such a simple case as the alloys of gold and silver, are very scanty. The complete proportionality which exists between density and composition by volume (or between specific volume and composition by weight) seems to exclude any important differences in the closeness of packing. There remains a difference in the attractive forces between the atoms—what is usually called internal pressure, and even here it is not easy to realise why the attractive force between gold and silver should be twice as great as between gold and gold or between silver and silver. A distortion of the space-lattice, producing a more or less irregular arrangement,

is only compatible with the conservation of the original density on the assumption of some form of packing which is not the closest possible. It would therefore seem that the solution of the problem must be sought from the crystallographers, whose newly added resources enable them to determine the direction of the planes of closest packing within a crystal, and the actual form of the space-lattice.

(B). NOTE ON CRYSTAL TWINNING AND THE MARTENSITIC STRUCTURE.

By Dr. CECIL H. DESCH (Glasgow).

THE present note deals with certain points in the paper communicated to the Spring Meeting of the Iron and Steel Institute by Professors Edwards and Carpenter, and with some experiments undertaken as a result of the discussion on that paper. One of the conclusions drawn by the authors on that occasion was that martensite and austenite were constitutionally identical, and differed only in the repeatedly twinned structure of the former. The hardness of martensite was attributed to the formation of amorphous material at the surfaces of slip on which twinning occurs. The so-called "acicular" structure of certain quenched aluminium-copper alloys was also regarded as due only to twinning. The structure of these alloys is distinctly "martensitic," and the analogy between them and the martensitic steels is undoubtedly a close one.

It is difficult to believe that the only difference between austenite and martensite lies in the repeatedly twinned structure of the latter constituent, accompanied by the formation of amorphous material. As Prof. Benedicks and Dr. Stead, among others, have pointed out, distinct differences are observable in the behaviour of the two constituents when present together in the same specimen of steel, and in the change of volume which occurs when austenite is cooled in liquid air. Hannemann has also shown reason for believing that austenite and martensite behave differently when resolved by annealing.

The present writer has never accepted the hypothesis of a hard modification of iron, and has always regarded the hardness of martensite as being connected with a partial resolution of austenite. That the resolution should proceed along gliding and twinning planes by preference is only in accordance with the usual behaviour of solid solutions, as evidenced by the formation of the Widmanstätten structure when such solid solutions undergo partial resolution (see paper by N. T. Belaiew in *Journ. Inst. Metals*, 1914, xii., and Discussion), and by the fact that corrosion proceeds preferentially along twinning planes (S. Whyte and C. H. Desch, *Ibid.*, 1914, xi., 235). Narrow twins (Neumann's lines) are readily developed in many metals. Professors Edwards and Carpenter have instanced the case of tin. Bismuth is also a convenient material for exhibiting the effect. Fig. 1 shows a portion of a crystal grain in a small ingot of cast bismuth, every grain of which is traversed by numerous Neumann's lines, as well as by broader and less regular twin lamellæ. In cast zinc the lines may be so closely packed and so narrow as to simulate very closely the structure of martensite. Whether these lines owe their origin to casting strains or to strains produced in cutting and filing the ingot is not decided, and there is no evidence that the abundance of very narrow twin lamellæ is accompanied by increased hardness.

The presence of a martensitic structure without increase of hardness is illustrated by Figs. 2, 3, and 4, which represent fields from a piece of overheated steel. A piece of steel plate, 0.28 per cent C., was heated to a white heat in a coke fire, and allowed to cool down with the furnace. A very coarse structure, like the Widmanstätten structure but with less regular outlines, was developed. The ferrite cell-walls were fringed with ferrite (Fig. 3), and the

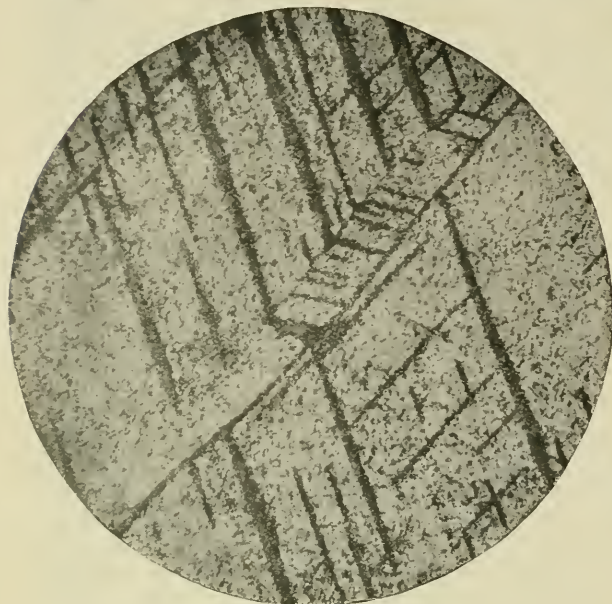


FIG. 1.—Twinning in Cast Zinc.

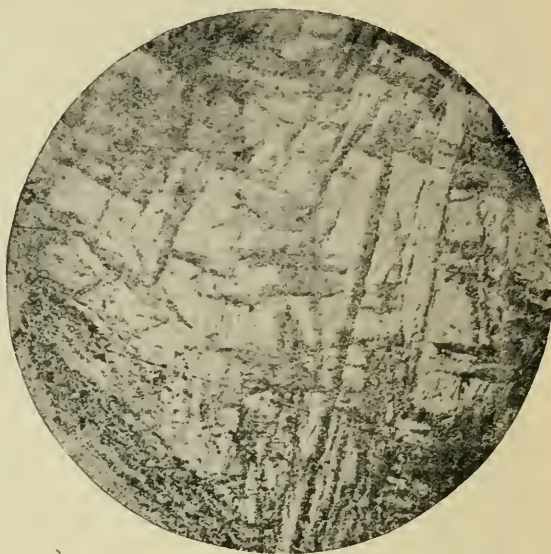


FIG. 2.—Martensitic Structure in slowly-cooled Pearlite.



FIG. 3.—Ferrite Fringe and Pearlite showing Martensitic Structure.

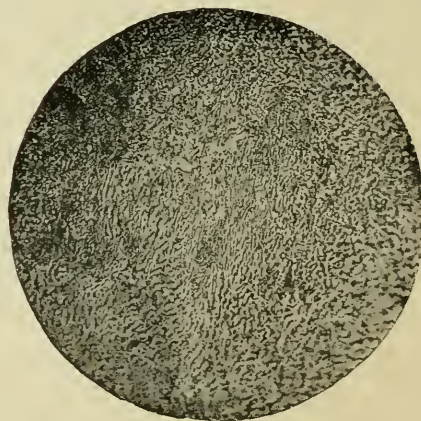


FIG. 4.—Pearlite in same specimen with 2 mm. Objective of 1.4 NA.

pearlite areas exhibited a remarkable pseudo-martensitic structure (Figs. 2 and 3), which had all the appearance of coarse martensite. Tested with a needle it proved to be quite soft, as might have been expected from the very slow cooling. Examined with an immersion objective the whole mass proved to be made up of pearlite (Fig. 4), closely packed in some parts and more loosely in others.

Such a structure may, of course, be regarded as pseudo-morphic after martensite, but it is impossible for the martensitic structure to have been produced by anything of the nature of chilling. The writer is inclined to take the view that resolution of the original austenite takes place most readily along gliding and twinning planes, and that

the distribution of the pearlite in the slowly cooled specimen records the earlier stages of the resolution. On this view, the martensitic structure of a quenched steel is an accompaniment and not the cause of its hardness. The writer is aware that this suggestion does not provide any explanation of the hardness of martensite, but only opposes the view that that hardness is due to twinning. Martensite is so much harder than its components as to suggest the presence of a solid solution, but whether that solid solution be a distinct phase, not yet recorded in the equilibrium diagram, or an unusual type of highly strained solid emulsion, remains doubtful.

The investigation of the distribution of pearlite in a slowly cooled steel is being continued.

RADIUM.*

(Continued from p. 286).

APPENDIX I. (continued).

THE Colorado carnotite deposits were apparently first noted as far back as 1881, when Andrew J. Talbert mined some of the ore and sent it to Leadville, where it was reported as carrying 5 dols. in gold per ton. This must have been an unusual ore as the carnotite now found does carry the precious metal. In 1896, Gordon Kimball and Thomas Logan sent specimens to the Smithsonian Institution, Washington, D.C., and were informed that the minerals contained uranium. Shortly thereafter they mined 10 tons of ore, shipped it to Denver, and sold it for 2700 dols. on account of its uranium content. Three years later, in 1899, Poulot and Voilleque collected and sent to France specimens which were examined by Friedel and Cumonge, who recognised the existence of a new mineral and named it "Carnotite," in honour of M. Carnot then President of the French Republic. In 1900, Poulot and Voilleque leached carnotite ores at Cashin, in the Paradox Valley, to extract the uranium. They shortly after completed a small mill in the McIntyre district south of the Paradox, and in this project had the co-operation of James McBride, a mining engineer of Burton, Michigan. Their mill ran until 1902, and during that time produced 15,000 pounds of uranium oxide. The mill was started again in 1903 by the Western Refining Company, but ran only a year. Up to 1904, the mills appear to have been run wholly with the idea of obtaining the uranium and vanadium from the ore for no radium was extracted.

Shortly afterwards the Dolores Refining Company built a new mill a short distance from the old one, but after running for some years, this mill, too, shut down. In 1912, the American Rare Metals Company acquired the mill of the Dolores Refining Company and is now operating it, with the special purpose of obtaining radium from the ores. The first attempt to attract radium in this country appears to have been made by the Rare Metals Reduction Company, under the management of Stephen T. Lockwood, of Buffalo, N.Y. In September, 1900, Mr. Lockwood brought back from Richardson, Utah, samples of carnotite ore, and in 1902 he published (*Eng. Min. Jour.*, of September 27th) the first radiographic plate from products of American carnotite. In June, 1902, he received 500 pounds of specially picked high-grade ore from Richardson, Utah, and in May, 1903, as a result of experimental work on this ore, he incorporated what was probably the first American company to operate a plant to produce radium as one of its products. In October, 1903, the first experimental plant was constructed, and in April, 1904, the first 17-ton car of ore reached Buffalo from Richardson, Utah. The company obtained a fair percentage of extraction but the ore proved to be too low-grade, and the Richardson deposits were abandoned. No radium in concentrated form was put upon the market, although barium sulphate concentrates were produced.

The General Vanadium Company which, with the Radium Extraction Company, is a subsidiary of the International Vanadium Company of Liverpool, England, was formed in 1909 and began work in 1910, the same year that the Standard Chemical Company of Pittsburgh, Pa., entered the field. Since that time these two companies have been engaged in mining carnotite. The ores from the General Vanadium Company have been shipped almost entirely abroad, while the Standard Chemical Company has shipped several hundreds of tons of carnotite to its works at Canonsburg, Pa. While it was stated at the time of the advance announcement of the bulletin to be issued by the Bureau of Mines that one American company had actively entered into the production of radium no actual sale of American-produced radium could be

authenticated. Since that time, however, the Standard Chemical Company has entered the American markets.

Besides the American Rare Metals Company and the Standard Chemical Company, a third company—the Radium Company of America with mines near Green River, Utah—has undertaken the production of radium in its plant at Sellersville, Pa. There is, therefore, every reason to hope that more and more of our ores will be worked up at home.

Besides the companies already mentioned, a number of independent operators mine and ship carnotite from the Paradox region and for the main part send their ores to Hamburg. Among the more prominent of these may be mentioned—

T. V. Curran, Placerville, Colo.

W. L. Cummings, Placerville, Colo.

O. B. Wilmarth, Montrose, Colo.

David Taylor, Salt Lake City, Utah.

The costs of mining, and especially of transportation, are an important factor in the marketing of carnotite. The Green River deposits have a distinct advantage over the Colorado deposits in this respect, as they are nearer the railroad, but, as their ores do not average so high in uranium, this advantage is more apparent than real. The present costs of mining, sorting, and packing in the Paradox apparently vary from about 28 dols. to 40 dols. per ton. To this must be added an 18 dols. to 20 dols. hauling charge to Placerville, and, in most instances, an additional charge for burros from the mines to points that can be reached by wagon. The freight rate from Placerville to Hamburg *via* Galveston is 14 dols. 50 cents per ton, so that the average cost at present to the miner of laying down his ore at the European markets approximates 70 dols. per ton. The selling price varies with the uranium content but is by no means proportional thereto, since a premium is always paid for rich ores. Very recently, however, a decided improvement has taken place, and for 2 per cent ore the price is now around 2.50 dols. per pound for the contained uranium oxide delivered in Europe with an allowance of about 13 cents per pound for the vanadium oxide content, so that the 2 per cent ore will now bring in Hamburg about 110 dols. per ton. One per cent ore is now saleable, but unless this ore is taken from the dump, so that the mining cost may be disregarded, it will scarcely bear present transportation charges from the Paradox, although it is more than probable that it will soon be shipped regularly from the Utah field.

A price of 110 dols. at Hamburg for 2 per cent ore leaves a good margin of profit to the miner, as mining profits go, but when it is considered that this price represents only a little over one-sixth of the value of the radium content of the ore, and that from this fraction of the value the American miner has to meet the outlay represented by the investment, by mining costs, transportation and assay costs, and by losses in transit, it seems scarcely just that nearly five-sixths of the value should go to foreign manufacturers of radium, especially when the fact is considered that radium can be produced much more readily from carnotite than from pitchblende. There are two ways of reducing this difference between the actual value of the ore and the price that the miner receives. One is to hold our American ores for a higher price, and the second is to manufacture radium at home.

Large wastes are still taking place in the mining of carnotite, owing to the inability of the low-grade ores to bear transportation charges. As has already been pointed out, however, a distinct improvement in this respect has taken place within the last few months. The miners are beginning to realise the value of their old dumps and are attempting to save the low-grade non-shipping ore in such ways as will render its marketing possible when prices advance. The Bureau of Mines has done everything it can to impress the necessity of this truest kind of conservation upon the mine operator.

In addition there is prospect that most of the low-grade ores can be successfully concentrated by mechanical

* Report No. 214, presented to the House of Representatives, U.S.A., at the 63rd Congress.

methods, and experiments at the Denver office of the Bureau of Mines indicate that a concentration of four to one can be obtained. In this concentration, however, there are losses which could be prevented by chemical concentration, but at the present time it costs more to ship the necessary chemicals to the mines than it does to ship the ores to places where these chemicals can be cheaply obtained. It would appear, however, that mechanical concentration can save at least one-half of the material that is now going to waste.

Although, until recently, the manufacture of radium from carnotite has been carried on almost wholly in France and Germany, there appears to be no good reason why our American carnotite should not be treated at home. Carnotite is much more easily treated than pitchblende and the essential features of methods for its chemical treatment are well known, although much of the mechanical detail of operation has been kept secret. As the mechanical requirements, however, are those which any well-grounded chemical engineer should be able to solve, there seems to be no good reason why any of our carnotite ores should be shipped abroad, even at two or three times the present market price of the material. As before stated, the essential features of chemical methods of extracting radium from its ores are well known. As regards the principles involved, the methods have advanced little beyond the original method published by Debieure.

The methods for carnotite may be described best in the words of Soddy, in an extract from "The Chemistry of the Radio Elements," by Frederick Soddy, p. 45, published in 1911 by Longmans, Green, and Co.

"The most important operations in the working up of radium-containing materials are the solution of the materials, consisting usually of insoluble sulphates, and the separation of the halogen salts of the alkaline-earth group in a pure state, followed by their fractional crystallisation. The first operation is usually effected by vigorous boiling with sodium carbonate solution, filtering and washing free from sulphate. This is the well-known reaction studied dynamically by Guldberg and Waage, whereby an equilibrium is attained between the two pairs of soluble and insoluble sulphates and carbonates. Naturally the greater the excess of sodium carbonate the larger the proportion of insoluble sulphate converted into insoluble carbonate. In this operation it is advisable not to wash at once with water but with sodium carbonate solution until most of the sulphates are removed, as thereby the reconversion of the carbonates back into insoluble sulphates is largely prevented. In dealing with crude materials, for example, the radium-containing residues from pitchblende, it is often advantageous to precede this operation by a similar one, using a sodium hydrate solution containing a little carbonate which dissolves part of the lead and silica present. The carbonates washed free from sulphates are treated with pure hydrochloric acid which dissolves the alkaline earths including radium. From the solution the latter may be precipitated as sulphates by sulphuric acid and reconverted back into carbonates as before. Or sometimes more conveniently they may be precipitated directly as chlorides by saturating the solution with hydrogen chloride; this is a very elegant method of great utility in the laboratory, for the most probable impurities, chlorides of lead, iron, calcium, &c., remain in solution, and only the barium and radium chlorides are precipitated, practically in the pure state, ready for fractionation."

(To be continued.)

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 7th inst.; Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. His Highness Maharaja Gaekwar of Baroda, and Mr. Archer M. Huntington, were elected Members. It was announced that the Managers had elected Charles Scott Sherrington, M.D., D.Sc., F.R.S., Fullerian Professor of Physiology, for a term of three years, the appointment to date from January 13, 1915.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, December 3, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"The Thermophone, a New Form of Telephone." By M. DE LANGE.

"Hermann's Phenomenon." By Dr. G. S. WALPOLE.

At the boundary between two solutions of unequal specific conductivity a change of reaction is developed if a difference of potential be maintained between them. Alkali is liberated if the current passes from the better conducting solution to that not conducting so well; acid, if the current passes in the opposite direction. The amounts may be calculated from the potential gradients in the solutions on each side of the boundary, the time for which the difference of potential is maintained, the resistance constant of the vessel employed, the dissociation constant of water, and the known migration velocities of hydrogen and hydroxyl ions.

CHEMICAL SOCIETY.

(Concluded from p. 294.)

THE following communications have been received during the vacation:—

254. "The Preparation of Phenyl Benzyl Ether." By DAVID HENRY PEACOCK.

For the preparation of fairly large quantities of phenyl benzyl ether the ordinary method is neither convenient nor economical. According to Beilstein (3rd. Ed., II., 1049), the compound is prepared by the action of benzyl chloride on potassium phenoxide. The method usually employed is to dissolve 94 grms. (one molecule) of phenol in a concentrated solution of the equivalent quantity of potassium hydroxide, and then, after the addition of 128 grms. (one molecule) of benzyl chloride, and about 20 cc. of alcohol, to heat on a water-bath under a reflux condenser for four hours. The yield of crude phenyl benzyl ether is only about 70 grms. A great disadvantage of this method is that the benzyl chloride and solution of potassium phenoxide do not mix, and therefore that reaction only occurs at their common surface. The liquid does not boil on the water-bath, which again militates against intimate contact.

It was found that the addition of copper powder as a catalyst greatly improved the yield; the following summary of two experiments shows this:—

I. 9.4 grms. of phenol, 5.6 grms. of potassium hydroxide in 5.6 cc. water, 2 cc. of alcohol, and 12.8 grms. of benzyl chloride heated on a water-bath for four hours—yield, 6.5 grms.

II. Same quantities as in I., but 0.1 gm. of copper powder added—yield, 10.1 grms.

The final method of preparation adopted was the following:—

Four hundred and seventy grms. of phenol were dissolved in a solution of 280 grms. of potassium hydroxide in 300 cc. of water. This was heated to about 80°, and a mixture of 500 grms. of benzyl chloride, 80 cc. of alcohol, and 0.5 gm. of copper powder added with frequent shaking. The mixture was heated under reflux in an oil-bath at 105–115°. It reacted vigorously at first, and was then kept in gentle ebullition for three hours. The non-aqueous layer was washed with warm water, dissolved in ether, and the solution dried. On removal of the ether and fractional distillation of the residue, 73 grms. of benzyl chloride were recovered and 575 grms. of phenyl benzyl ether obtained, a yield of about 90 per cent of the theoretical, calculated from the benzyl chloride consumed.

Phenyl benzyl ether can be economically purified by fractional distillation under a pressure of 60–80 mm.

The method described above would obviously be applicable, after suitable modification, in the preparation of ethers of substituted phenols, using other halogen derivatives than benzyl chloride.

255. "The Capillary Constants for Liquid Carbon Monoxide and Liquid Argon." (A Correction). By C. A. CROMMELIN.

Whilst making calculations some time ago concerning the capillary constants of argon (Mathias, Onnes, and Crommelin, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, xv., 667, 960) errors were found in the tables of data given by Baly and Donnan in their paper on the surface-energies and densities of some liquefied gases (*Trans.*, 1902, lxxxi., 907).

Below are given the corrected data for the surface-tensions of argon and carbon monoxide. Dr. G. Rudolf has already (*Ann. Physik.*, 1909, [iv.], xx., 751) published the corrections for argon, but the complete tables for carbon monoxide and argon are conveniently given here.

TABLE XVIII. (corrected).
Surface Tensions of Liquid Carbon Monoxide.

T	70	71	72	73	74	75	76	77
γ	12.11	11.88	11.64	11.41	11.18	10.96	10.73	10.50
T	78	79	80	81	82	83	84	85
γ	10.28	10.05	9.83	9.61	9.39	9.17	8.96	8.74
T	86	87	88	89	90			
γ	8.53	8.31	8.10	7.89	7.69			

TABLE XIX. (corrected).
Surface Tensions of Liquid Argon.

T	..	84	85	86	87	88	89	90
γ	..	13.45	13.19	12.93	12.68	12.42	12.17	11.92

The γ -values for oxygen and nitrogen are correct.

256. "p-Chlorophenylselenious Acid." (Preliminary Note). By GILBERT T. MORGAN and J. CAMPBELL ELLIOTT.

p-Chlorophenylselenocyanate, $C_6H_4Cl \cdot Se \cdot CN$ (yellow leaflets from alcohol, m. p. 50–51°), was obtained by adding an alcoholic solution of potassium selenocyanate to a well-cooled aqueous solution of p-chlorobenzenediazonium chloride containing excess of sodium acetate. The cyanide group was readily removed by the action of aqueous alkali hydroxide, and the resulting selenophenol, $C_6H_4Cl \cdot SeH$, oxidised to the diselenide, $(C_6H_4Cl \cdot Se)_2$, by hydrogen peroxide. Oxidation of either of these compounds with alkaline permanganate gave rise to sodium p-chlorophenylselenate.

p-Chlorophenylselenious acid, $C_6H_4Cl \cdot SeO_2H$ (colourless needles from hot water, m. p. 178°), was produced by boiling the preceding sodium salt with hydrochloric acid; it is an amphoteric substance, giving rise to metallic p-chlorophenylselenites and to salts of the mineral acids, such as the nitrate and hydrochloride. A more detailed examination of these aromatic selenium derivatives is in progress.

257. "Benzenesulphonyl Derivatives of o-Aminoazo-compounds." (Preliminary Note). By GILBERT T. MORGAN and JOHN HARBOURNE COOKE.

Benzenesulphonyl derivatives of aromatic o-diamines condense readily with aromatic nitroso-hydrocarbons in acetic acid solution, furnishing azo-derivatives.

4-Benzenesulphonyl-3:4-tolylenediamine and p-nitrosotoluene give rise to 4-benzenesulphonyl-4-amino-3-azotoluene (I., golden-yellow needles, m. p. 151–152°). 3-Benzenesulphonyl-3-amino-4-azotoluene (II., dark yellow

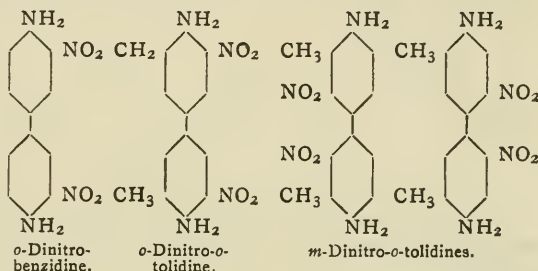
needles, m. p. 156°), produced similarly from 3-benzenesulphonyl-3:4-tolylenediamine, is an acyl derivative of the still unknown 3-amino-4-azotoluene.

Experiments on the hydrolysis and oxidation of these azo-derivatives are in progress.

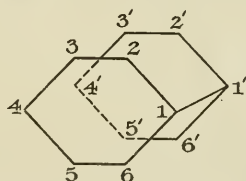
258. "The Possibility of a New Instance of Optical Activity without an Asymmetric Carbon Atom." By HAROLD KING.

Up to the present time the only experimentally realised instances of optical activity in the absence of an asymmetric carbon atom are furnished by Perkin, Pope, and Wallach's (*Trans.*, 1909, xcvi., 1789) resolution of 1-methylcyclohexylideneacetic acid, and Mills and Bain's (*Trans.*, 1910, xcvi., 1866) resolution of the oxime, and later of other simple derivatives of cyclohexanone 4-carboxylic acid. The molecular asymmetry of such substances belongs to the centro-asymmetric type.

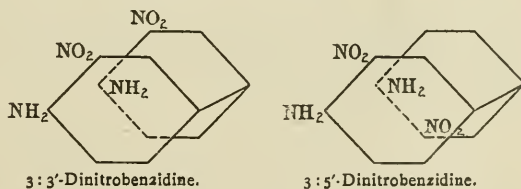
The possibility of further examples of the centro-asymmetric type, differing widely from the previously known cases, is perceivable from the discovery by Cain and his co-workers of two o-dinitrobenzidines, two o- and four m-dinitro-o-tolidines of the formulæ shown below, each representing two isomerides:—



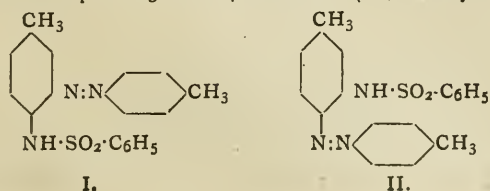
To explain the existence of these isomeric dinitrobenzidines and dinitrotolidines, Cain and Micklethwait (*Trans.*, 1914, cv., 1437) adopt Kauffner's spacial diphenyl formula as the basis:—



On this assumption the two o-dinitrobenzidines, for example, are formulated thus:—

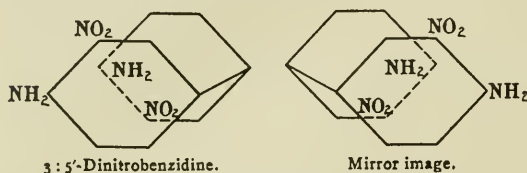


where the two planes of the benzene rings are superimposed, but not necessarily parallel to each other. The isomerism is ascribed to the non-rotation of one of the benzene rings. In the particular instance cited, Cain and Micklethwait have been unable to effect interconvertibility of the isomerides by any means, indicating the difficulty of free rotation of one of the rings relative to the other. A transformation, however, has possibly been effected in the case of the two o-dinitrotolidines. Now, Cain and Micklethwait find their difficulty in that they are quite unable to fix the orientation respectively of these pairs of isomerides; for example, in the case of the dinitro-

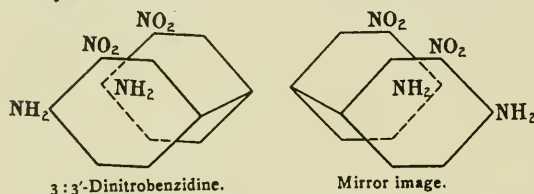


benzidines they have no means of proving which is the 3:3'- and which the 3:5'-isomeride.

It occurred to the present author, however, that one of each of these pairs of isomerides presents a new instance of the centro-asymmetric type of enantiomorphous compound capable of resolution into its optically active isomerides. That such a possibility exists, is evident from visual examination of the configurations of 3:5'-dinitrobenzidine and its mirror image:—



These configurations are unquestionably not identical in that they are not superimposable. 3:5'-Dinitrobenzidine should therefore be capable of resolution into its optically active isomerides. On the other hand, 3:3'-dinitrobenzidine is identical with its mirror image, as can be readily seen:—



3:3' Dinitrobenzidine is therefore unresolvable. It should be emphasised that these deductions are only valid if the underlying principle of Kaufler's spacial formula is accepted.

On the basis of the acceptance of Kaufler's formulæ for diphenyl and for other polycyclic systems, the above considerations are capable of wide extension.

259. "Note on the Dilution Law." By JAMES RIDDICK PARTINGTON.

The empirical dilution law published by Kendall (*Trans.*, 1912, ci., 1275):—

$$\frac{c\gamma^2}{1-\gamma} = K + k \frac{1-\gamma}{\gamma} \dots (1)$$

is identical with that proposed two years previously by the author on theoretical grounds (*Trans.*, 1910, xcvi., 1158), which may be written in the form:—

$$\frac{c\gamma^2}{1-\gamma} = A + B \cdot c\gamma \dots (2)$$

where A and B are constants.

The second term on the right of each equation is a correction term, in the transformation of which it is legitimate to apply Ostwald's dilution law:—

$$\frac{1-\gamma}{\gamma} = K'c\gamma \dots (3)$$

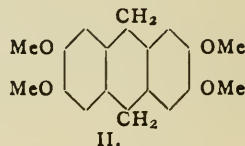
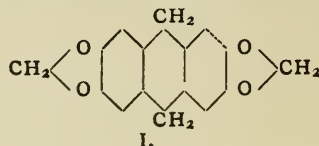
Thence, if $k = BK'$, equations (1) and (2) are identical.

260. "A Reaction of Homopiperonyl and of Homoveratryl Alcohol." (Preliminary Note). By GERTRUDE MAUD ROBINSON.

In 1909 Ewins (*Trans.*, xcv., 1486) observed that homopiperonyl chloride readily underwent condensation under the influence of phosphorus pentachloride, yielding an almost insoluble substance, which he regarded as a dihydroanthracene derivative of the formula I. Owing, however, to the impossibility of oxidising it to an anthraquinone and to other experimental difficulties, it was not found possible definitely to prove this view.

Having had occasion to employ homopiperonyl alcohol in connection with another investigation, the present author

has observed its extreme sensitiveness to the action of acids which convert it into the substance described by Ewins. It was also found that homoveratryl alcohol, obtained with hydroveratrol by the reduction of veratraldehyde with sodium amalgam in aqueous-alcoholic solution, undergoes an analogous reaction, for example, on being warmed with a solution of sulphuric acid in glacial acetic acid. The product in this case is 2:3:6:7-tetramethoxydihydroanthracene (II.), which is a more amenable substance than the piperonyl derivative, and was accordingly chosen for a more detailed investigation:—

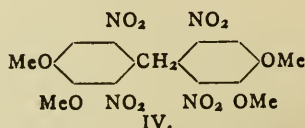
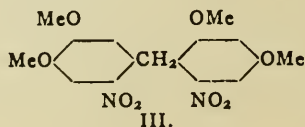


It is sparingly soluble in alcohol and crystallises best from benzene in slender colourless needles melting at 227° and capable of distillation without decomposition. This substance is also obtained when veratrole is condensed with formaldehyde by means of 60 per cent sulphuric acid, and this method was adopted for the preparation of the compound.

On demethylation with boiling hydriodic acid, followed by distillation of the product with zinc dust, 9:10-dihydroanthracene was obtained, whilst oxidation by heating with litharge yielded 2:3:6:7-tetramethoxyanthracene, a substance which crystallises from ethyl acetate in colourless prisms melting at about 135°, and containing a molecule of solvent of crystallisation, or from alcohol in colourless needles melting at 173° and free from solvent. The dihydroanthracene is not fluorescent, whilst the corresponding anthracene derivative exhibits intense blue fluorescence in all its solutions.

On oxidation of 2:3:6:7-tetramethoxydihydroanthracene with 40 per cent nitric acid, 4:5-dinitroveratrole and 6-nitroveratric acid were isolated, whilst more careful treatment with nitric acid in acetic acid or acetic anhydride solution resulted in the production of a substance, $C_{17}H_{18}O_8N_2$, which crystallises from acetic acid in pale yellow needles melting at 183°. This proves to be 6:6'-dinitro-3:4:3':4'-tetramethoxydiphenylmethane (III.), and its production involves the replacement of a methylene by two nitro-groups.

This derivative, on further boiling with nitric acid, yields a certain amount of dinitroveratrole and 2:2':6:6'-tetranitro-3:3':4:4'-tetramethoxydiphenylmethane (IV.) as the main product. The latter substance crystallises from ethyl acetate in pale yellow rhombic prisms, melting at 210°, and sparingly soluble in most organic solvents:—



Ewins (*loc. cit.*) treated dimethylenetetraoxydihydro-

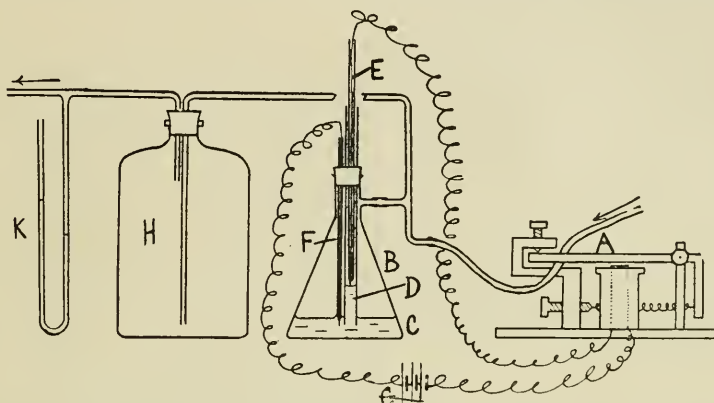
anthracene with nitric acid, and obtained a product melting at 217° , for which he did not suggest a constitution. His analytical results agree excellently with the assumption that the substance is $C_{15}H_{10}O_3N_2$, and constituted analogously to the above-described dinitrotetramethoxy-diphenylmethane.

261. "The Preparation of 3-Nitro-o toluidine." By JOHN HENRY HADFIELD and JAMES KENNER.

Considerable quantities of the above compound were required with a view to its conversion into 3-nitro-2-chlorobenzoic acid, the reactions of which it was desired to investigate. The preparation of the base according to the process described by Gnehm and Blumer (*Annalen*, 1898, ccciv., 105) was, however, found to be inconvenient owing to the readiness with which decomposition set in. Systematic experiments, based on Wülfing's method for the preparation of o-nitroaniline (D.R.P. 65212, 66060),

The electro-magnet is put in series with E, F, and a battery G, so that when the gas-pressure forces the conducting acid up D, the circuit is closed, the electro-magnet excited, and the gas cut off. Any desired pressure is easily obtained by adjusting the height of E. The regulator appears to work equally well with low and high pressure in the gas main. The apparatus figured has been in use for more than a year; with an electro-magnet having a resistance of about 100 ohms, a 6-volt battery is sufficient, and the current used is very small. A weight may be with advantage put on the hinged bar, oscillations in pressure being considerably reduced by its means. The regulator in use is arranged to keep the pressure at 5 cm., the amplitude of the oscillations being only in the neighbourhood of a millimetre.

(We are indebted to the Chemical Society for permission to reproduce the accompanying woodcut).



were, therefore instituted, and the following procedure was finally adopted:—

A mixture of oxalo-o-toluidide (18 grms.) with concentrated sulphuric acid (96 grms.) was heated on the water-bath until a test portion was completely soluble in water. The product having been cooled to 50° , a mixture of nitric acid (D 1.42; 12 grms.) with sulphuric acid (12 grms.) was gradually added, the whole being well shaken and cooled to prevent any rise in temperature above 50° . After the pale red mixture had remained for some hours at the ordinary temperature, water (50 cc.) was added, and the product was then heated in a reflux apparatus by means of an oil-bath at 140° until solution was complete. The temperature of the bath was then raised to 150° , and the heating continued for fifty minutes. The solution was then considerably diluted, and the base removed in a current of steam. In this manner 8.5 grms. of base were obtained.

262. "Note on a Gas-pressure Regulator." By ALFRED FRANCIS JOSEPH.

The regulator described was designed for use with a high and unsteady gas pressure (about 20 cm. of water); it can be used to reduce to any desired pressure down to a few millimetres.

The gas from the main enters through a thin-walled rubber tube, which passed between a fixed point and the hinged bar of an electro-magnet, A (an old telegraph sounder was used). By means of a T-piece the tube is connected to a filter flask, B, containing 40 per cent sulphuric acid, C. D is a tube about 1 cm. in diameter fitting the stopper of B tightly, and E a narrow tube passing loosely into B, and provided with a platinum point and mercury contact; the height of the platinum point above the level of the acid can be adjusted. F is another narrow tube with platinum point. H is a large bottle to take up small variations of pressure, and K a water manometer.

NOTICES OF BOOKS.

Technical Gas Analysis. By GEORGE LUNGE, Ph.D., Dr. Ing. (H.C.). London: Gurney and Jackson. 1914.

MODERN methods of technical gas analysis are comprehensively discussed in this book, a special feature of which is the number of references given in it to the literature of the subject. The chief desideratum of technical as opposed to scientific analysis is, of course, rapidity, and the author has been careful to pay the fullest attention to those methods which can be carried out in the shortest possible time with the degree of accuracy required for their purpose. The use of modern apparatus for technical gas analysis and general methods of absorption, combustion, &c., are first fully described, before the application of them to gases commonly occurring in technical operations is treated. The outstanding features of the book are those which the scientific world is now accustomed to associate with Dr. Lunge's name—accuracy, comprehensiveness, and attention to detail—and chemists working on gas analysis will undoubtedly find it of very great use.

The Electrical Conductivity and Ionisation Constants of Organic Compounds. By HEYWARD SCUDDER, B.A., B.S., M.D. London: Constable and Co., Ltd. 1914.

THE object of this book of tables is to give a complete bibliography of all the measurements of the ionisation constants and the electrical conductivity of organic compounds which have appeared in periodical literature between the years 1899 and 1910 inclusive, together with the values of the ionisation constants and some of the values of the electrical conductivity. Seventy-eight journals and about 5000 dissertations have been examined

page by page, and the indexes of other journals have also been searched. The tables are well arranged, and both an author list and a formula index are provided. The value of a book of tables depends mainly upon its completeness, the convenience of the arrangement adopted, and its accuracy. About the first two of these desiderata there can be no question, while as far as can be tested otherwise than by constant use the information given seems to be quite reliable.

The British Pharmacopœia, 1914. London: Constable and Co., Ltd. 1914.

THE General Medical Council announces that advance copies of the *Pharmacopœia* for 1914 are now ready, and may be seen by the public from ten to four daily (Saturdays 1 p.m.) at 299, Oxford Street, London; 54, George Square, Edinburgh; and 35, Dawson Street, Dublin. Thus manufacturers, pharmacists, and others interested can ascertain the changes that are about to be made in official requirements, and can make the necessary arrangements to meet them. Every person who takes advantage of this opportunity will be expected to sign a declaration to the effect that he will not publish any substantial extracts from it without the Council's sanction, nor publish in book form before December 31, 1914, any information derived from the new issue. No objection will be taken to such reasonable references to the facts and figures in it as may properly be made for purposes of criticism, review, or summary.

In the new issue the metric system has been employed for all pharmaceutical and analytical computations, and for the specification of doses, which are also expressed in terms of the imperial system. Descriptions of methods of preparation have been considerably shortened, while those of tests have been amplified and increased in number.

An Introduction to the Study of Physical Metallurgy. By WALTER ROSENHAIN, B.A., D.Sc., F.R.S. London: Constable and Co., Ltd. 1914.

DEFINING physical metallurgy as the study of the physical aspects of metals and of the nature, properties, and behaviour of single metals and alloys, the author of this book has given a general survey of the subject, based upon the investigation of metallic structure and constitution. The book is a valuable addition to scientific literature, and it is to be hoped that its publication will awaken the interest of engineers and users of metals, and induce them to avail themselves more freely of the data which the methods of physical metallurgy have accumulated. The first part contains accounts of the microscopes and instruments employed, with general information relating to their use and the results obtained with them. A special chapter is allotted to the iron-carbon alloys. In the second part the mechanical testing of metals, the effects of strain, and the causes of defects and failures are treated. Most of the micrographs with which the book is illustrated have been taken from the author's own work or from that of members of the staff of the Metallurgical Department of the National Physical Laboratory. The practical value of the new science of physical metallurgy can hardly be overestimated, and this book, besides giving engineers a knowledge of the results which have been obtained, should also stimulate the investigation of many highly important questions.

The Chemical Examination of Water, Sewage, Foods, and other Substances. By J. E. PURVIS, M.A., and T. R. HODGSON, M.A. Cambridge: The University Press. 1914.

THIS book belongs to the Cambridge Public Health Series, and is written for students attending courses for the diplomas and degrees in public health. Working

directions are given in it for qualitative and quantitative tests of water, foods, &c., and many typical results of analyses of all kinds of samples are included. The ordinary routine methods adopted by public analysts are usually described, but when it appears desirable a choice of methods is given, and the interpretation of results is always fully described. The detection and in some cases the estimation of common adulterants of various articles of food is included, and in every respect the book may be regarded as a satisfactory introduction to food analysis.

CORRESPONDENCE.

WAR ON GERMAN TRADE IN BELGIUM.

To the Editor of the Chemical News.

SIR, Through the columns of your valuable paper may we draw the attention of English manufacturers to the splendid opportunity they have at present in making arrangements to be represented in Belgium.

Amongst the good class of refugees there are a number who, before the war, acted for German firms, and who are wishful to replace these makers by English manufacturers of similar goods.

These refugees are here unoccupied, and would be very pleased to spend their time in acquiring the knowledge of the lines they will be called upon to introduce later on.

The Belgian Chamber of Commerce in London, 24, St. Dunstan's Buildings, St. Dunstan's Hill, E.C., is at the disposal of manufacturers to put them in communication with suitable applicants for such posts. We further take advantage of the present to invite all employers who have vacancies for foreign correspondents, &c., to let us have particulars of their requirements, as the enforced idleness is very irksome to our countrymen.—I am, &c.,

L. GODCHAUX, President.

Belgian Chamber of Commerce in London,
24, St. Dunstan's Buildings,
St. Dunstan's Hill, E.C.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clix., No. 19, November 9; No. 20, November 16; No. 21, November 23, 1914.

These numbers contain no chemical matter.

No. 22, November 30, 1914.

Indene Dicarboxylic and Hydrindene Dicarboxylic Acids.—J. Bougault.—When concentrated sulphuric acid acts on benzyloxalacetic ether a product of formula $C_{15}H_{17}O_4$ is obtained. This is the diethyl ether of indene dicarboxylic acid, and the acid itself may be obtained from it by acid saponification. This new acid is almost insoluble in water, benzene, and acetic acid. It dissolves in alcohol and acetone. It decomposes at about 215° , giving CO_2 and indene carbonic acid. When hydrogenated with zinc in acetic solution it gives hydrindene dicarboxylic acid. This acid fuses at 222° without undergoing decomposition. It is more soluble in most solvents than indene dicarboxylic acid.

THE CHEMICAL NEWS.

VOL. CX., No. 2874.

THE "SULPHATE" IN RIVER WATERS.

By H. S. SHELTON.

IT is somewhat unusual to wait more than three years before replying to criticism. My excuse in the present instance is that I was unaware that any had been published. So far as I can discover, no one has attempted to inform me of its existence, and although I have from time to time communicated with many prominent chemists on the matter dealt with in this article, all of them were, seemingly, as ignorant as myself. I am now indebted to Prof. F. W. Clarke for the necessary information. The present paper is a reply to an article by Mr. R. B. Dole, which appeared in the *CHEMICAL NEWS* (1911, ciii., 289) under the title "The Occurrence of Sulphates in River Waters," which paper is solely concerned with criticisms of my "Correlation of Rock and River Water Analyses" which appeared in the *CHEMICAL NEWS* (1910, cii., 75). As the criticism is "Published by permission of the Director, United States Geological Survey," it is to be assumed that the views expressed commend themselves to others engaged in geochemical work.

My original essay called attention to a remarkable discrepancy in geochemical data. The admirable series of rock analyses carried out by the U.S.A. Geological Survey and the careful statistical manner in which the results have been tabulated elucidates the remarkable fact that sulphur, so far as the crust of the earth is concerned, is a minor constituent, amounting to less than 0.2 per cent of known strata. I also showed clearly that this amount was wholly inadequate to account for the large proportion of sulphate stated to be present in river waters. I inferred therefrom that there was a considerable error either in the sulphur determinations of rock analyses, or in the sulphate determinations of river water analyses, or in both.

With regard to the discrepancy, my critic, on the one hand, calls it an "alleged discrepancy," on the other hand he remarks that "the source and ultimate disposal of sulphates in river waters may be obscure to the casual observer." Whether he is to be regarded as a casual observer is an open question; at any rate he gives us no idea whatever what his own theory may be of its source or its disposal, and makes no attempt to answer the main contention of my paper, that the discrepancy is great and glaring. In the present paper, therefore, I shall assume that the discrepancy exists, and devote myself entirely to Mr. Dole's attempt to substantiate the accuracy of the river water analyses. It is, however, desirable to emphasise the starting point of the investigation. If water analysts inform us that large quantities of calcium carbonate are continually carried down to the sea in river waters there is no reason for disputing the statement. There is no mystery either about the source or the disposal of calcium carbonate. Should, however, an analyst inform us that the soluble contents of river water were mainly ammonium molybdate and platinum chloride, there would be good reason for doubting the accuracy of the analyses. It is for a similar reason that I have disputed the accuracy of the sulphate analyses of river waters. The reason is that there is no adequate source for the alleged sulphate, and, moreover, there is no known means by which the alleged sulphate, when it reaches the sea, can get out again. The statistics in my original paper, I think, abundantly prove this statement. I shall, however, shortly publish further statistics placing the matter entirely beyond dispute. The present paper is concerned with Mr. Dole's contention that the determinations of sulphates in river waters are so well established as to be indisputable.

The theory suggested in my paper was that the "sulphate" was probably some other substance with a barium salt, insoluble in hydrochloric acid. My critic mentions the contention, but makes no reply to it whatever. The careful description of the method of work carried out in the U.S.A. Geological Survey laboratories substantiates rather than disproves the probability. It will be well therefore to examine Mr. Dole's arguments *seriatim*.

It is stated that Prof. F. W. Clarke's statistical estimate of the quantity of sulphate is greater than the one of Sir John Murray quoted by me. The statement is one I am prepared to accept. Prof. Clarke's averages have as their basis a large number of analyses not included by Sir John Murray, and a larger number carried out since Sir John Murray's paper was published. There is therefore every reason to assume that Prof. Clarke's average of the data is more accurate. The average proportion of SO_4 stated to be present in river waters is 12 per cent, not 8 per cent as stated by Sir John Murray. The discrepancy to which I alluded is all the more striking.

The method adopted by the analysts of the U.S.A. Geological Survey is described in detail. The principal difference between the method used and that described by me is that, before the analysis of the dissolved matter, the filtered water is evaporated to dryness in a platinum vessel on a water-bath, and dried at 180°C . for one hour. Mr. Dole appears to think that the treatment is such as to negative my suggestion, and remarks that it "precludes great error by retention of silicates or organic compounds in the precipitate." With this statement I shall deal presently, but first I will make one criticism. The method renders much more probable one source of error previously mentioned by me. It is a fact well recognised by the older river and rain water analysts that sulphate determinations are specially liable to error through the absorption of sulphur-dioxide from the fumes of the gas used in evaporating the water. Warington in particular (*Journ. Chem. Soc.*, 1889, p. 545) is careful to warn analysts of this error, and to point out that in the absence of special precautions very inaccurate analyses were liable to be made. This was written when it was not customary to evaporate to dryness. I have not yet been able to refer to the sources of error pointed out by Mr. Hillebrand, but I venture to point out that Mr. Dole's method is such as to accentuate one that has always been recognised by the best water analysts. The evaporation is, it is presumed, carried out over a constant level water-bath heated in the usual way by the Bunsen. The evaporation would take considerable time, and there is every opportunity for the varying air currents to convey minute traces of SO_2 to the slowly evaporating liquid. Moreover, the prolonged heating at 180°C . would ensure the oxidation of any sulphite formed. Whatever sources of error Mr. Dole's method may eliminate this is undoubtedly one that is liable to be increased.

The suggestion that considerable error from retention of silicates or organic compounds is avoided by heating to 180° is highly disputable. I am, of course, aware that the silica in such a compound as sodium silicate is thrown into an insoluble form. Indeed, I am somewhat surprised that a portion of the aluminium is not thereby mixed with the silica. Mr. Dole, however, assumes too much if he states dogmatically that all silicon compounds are reduced to silica at that temperature, or that all organic compounds are decomposed. Indeed, both the latter statements are obviously wrong. That silicates or organic compounds, or both, cannot survive at 180° , and cannot afterwards be precipitated by an acid solution of barium chloride is a statement that requires definite experimental proof. My own suggestion in a previous paper was organosilicate, the presence of which in river waters has been asserted by Thénard. Prof. Clarke has recently rejected Thénard's work, but the reasons for so doing are not sufficiently clear. I am not committed to that particular suggestion, though I think it deserves careful investigation. The point that

requires emphasis is that neither Mr. Dole nor anyone else has given a sufficient reason, or, indeed, any reason whatever, why the precipitate must necessarily be barium sulphate.

Mr. Dole mentions an instance of a river with small drainage area, the sulphate of which is referred to a deposit of bituminous shale associated with a coal-bed. It is no part of my case to deny that, in exceptional instances, there may be a considerable amount of true sulphate in river water. Mineral springs of unusual composition are discovered from time to time. Nor have I at any time denied that some sulphate is present normally. My previous paper did, I think, clearly prove that the amounts calculated by Sir John Murray and Prof. Clarke are certainly not there. Such a quantity can neither be referred to any known source, nor is there any known means by which the sulphate, when it reaches the sea, is returned to the sedimentary rocks. The proportion of sulphate in any particular river water is a matter for experimental investigation, and it is not possible without detailed work definitely to say in any particular instance that the analysis is wrong. I do, however, regard with extreme suspicion such a result as 100 parts per million SO_4 for the Missouri, or 26.4 per cent of total solid for the Mississippi at Memphis. In such a case the probability of error is very great.

I have thought it desirable to keep my reply to Mr. Dole distinct from original work and positive suggestions. The above remarks cover nearly everything he has said except his claim to have completely refuted my contention that sulphates are grossly over-estimated. Needless to say he has done nothing of the kind. He has merely stated, what no one has denied, that river water analysts obtain a precipitate on treating the soluble part of the residue obtained by evaporation of a small quantity of river water with barium chloride in acid solution. The natural presumption is that the precipitate is barium sulphate. If there were no sound reason to the contrary, there would be something to be said for the custom of calling the precipitate sulphate without further investigation. I have, however, given very cogent reasons for thinking that further investigation is required. Mr. Dole not only makes it abundantly clear that such investigation has never been undertaken, but raises the suspicion that some proportion of the SO_4 may be due to an analytical error of the crudest kind. I am still of opinion that the precipitate obtained by treating with barium chloride is real, and is some other substance or substances than sulphate, probably complex silicates, but Mr. Dole's explanation shows that it is at least a matter for investigation whether it is not partly due to SO_2 obtained from the Bunsen flame.

The most surprising feature of Mr. Dole's paper is not so much his inability to make an effective reply to my arguments as the fact that, though a chemist on the staff of the U.S.A. Geological Survey, he has ignored the statistics I put forward to show the startling nature of the discrepancy. Had my paper been criticised by anyone ignorant of Prof. Clarke's statistical work and of its value and meaning, a number of criticisms would have been expected which are not possible to Mr. Dole. He solves the difficulty by saying nothing at all on the main question, and the *ignoratio eleuchi* is so patent as to seem almost wilful. What he has made clear, however, is that the bearing of the arguments I put forward in my previous article does not appear to be thoroughly grasped by analytical chemists. I propose therefore, shortly to publish further data on the matter.

Royal Institution.—Prof. Charles Scott Sherrington, M.D., LL.D., D.Sc., F.R.S., new Fullerian Professor of Physiology at the Royal Institution, will deliver a course of six lectures at the Institution on "Muscle in the Service of Nerve," on Tuesdays, January 19, 26, February 2, 9, 16, 23, 1915. Lecture hour, 3 o'clock.

THE SUPPLY OF CHEMICALS TO BRITAIN AND HER DEPENDENCIES.*

By Sir WILLIAM A. TILDEN, D.Sc., LL.D., F.R.S.

(Concluded from p. 294).

IN 1900 a lecture was delivered on the occasion of the opening of the Hofmann House in Berlin by Dr. H. Brunck, since 1884 chief technical Director of the Badische Company, on the "History of the Development of the Manufacture of Indigo." This lecture, in the form of the English version issued by Dr. Brunck, may be fairly regarded as a sermon preached to British manufacturers. Its perusal will convince anyone that the success which has been achieved is the reward of long sustained investigation in the laboratory of the scientific chemist, and to do justice to this conviction I wish every chemical employer in this country could be induced to read the weighty and eloquent words of the author. He would then perceive that to permanent industrial success there is only one road, and that the way pointed by science.

I will content myself with quoting only a passage or two from Brunck's lecture (pp. 4, 22).

"With grateful admiration and reverence do we recall those ever memorable masters, Kekulé and A. W. von Hofmann, whose gifted achievements have laid the foundations of our industry. And when we look back at all the technical achievements we also gratefully recall the fertile discoveries of Graebe and Liebermann, of Peter Griess, and the beautiful researches of Emil and Otto Fischer, of O. N. Witt and the numerous other investigations conducted in our university laboratories, which have acted as incentives for chemical industry, and have furnished the foundation for renewed progress. But first and foremost we are impressed by the mighty influence of the investigations of A. von Baeyer, to whom the coal-tar colour industry is indebted for a great number of important achievements, and who himself has, to-day, unfurled before you the picture of a magnificent scientific creation, from which it was possible for chemical industry to construct and develop one of its grandest achievements.

"But this infant industry was no longer content to be dependent on the gifts which were made to it from various scientific sources. Renowned investigators placed themselves entirely at the disposal of chemical industry; young men in great numbers devoted themselves to it, and grew up with it in enthusiastic and self-directed activity. Such men as Caro, Glaser, Martius, and later on Laubenheimer, Duisberg, Berntsen, and many others, introduced the spirit of scientific investigation into industrial practice." And, in conclusion, he says: "You have seen that this new industry is not an unexpected gift fallen from the heavens, but that in order to complete the task the intellectual labour and the industry of many men had to be co-ordinated in an organised attempt to attain a definite object for a number of years and throughout a considerable period when success could by no means be regarded as certain. The pre-requisites for practical indigo synthesis was supplied by the results of long years of scientific labour."

In the semi-annual report for April, 1903, issued by Schimmel and Co., the famous manufacturers of essential oils, there are some figures which show the increase of chemical works in Germany and the great increase in the numbers of qualified workmen employed therein, on which the firm makes the following remark:—"The foregoing figures show clearly that the German chemical industry has passed intact through the economic crisis of the last few years. Further, there are no grounds for fearing that it will be outstripped by competition from abroad, so long as the German universities possess such eminent representatives of chemical science."

It is now time to consider what ought to be done and what it is possible to do in this country to remove reproach

* Read before the Royal Society of Arts, November 25, 1914.

from British chemical industry, and to render the Empire independent of supplies from foreign sources.

We need many first-rate chemists, a few engineers, plenty of capital, and some good men of business. A combination of these elements in due proportion is certain of success, and the time, though so unhappy for the world, is favourable for this enterprise.

Inasmuch as the functions of each and the best way of combining them have already been settled in practice on the Continent, it is to be hoped that the ancient precept about being taught by the enemy—*jas est et ab hoste doceri*—will not be forgotten. For there can be no doubt that the principle acted on in all German chemical factories, namely, the employment of the best available scientific skill and the constant appeal to scientific research, has been the secret of their success.

In the British colleges and universities there are many able young chemists, but many more are required. Here education and industry interact on each other. If the demand for scientific assistance were more general, the supply of well-qualified men would soon be greatly increased, and greater attention given by the teachers to the industrial side of the subject. At present other professions in which the prospects are more alluring attract into other lines of work much of the talent of the country. This, however, is not to be interpreted as meaning that there is not now a supply of able young chemists sufficient for immediate needs. The difficulty is to induce chemical manufacturers to treat them reasonably. The pay offered is generally insufficient, and though conditions are somewhat improved of late years, the employer too often expects immediate profitable returns from the engagement of a scientific man. In the Badische works at Ludwigshafen the plan has been to engage university men on the recommendation of their professors for a term of years, at a salary which will enable the new members of the staff to live at least modestly. I am told that in some American works the same system has been adopted. These young men are placed in the research laboratory under the chief chemist controlling the department of manufacture selected, and it is not expected that they will accomplish anything very remunerative at first. But their future depends on their ability and activity, and they act accordingly.

Then there is the position to be accorded to the engineer. He is, of course, indispensable; but the part he should play in the works depends on the nature of the processes involved. So far as relates to buildings and other structures, to supplies of water, fuel, power, and electricity, the engineer has the field to himself, but the operations in which materials are to be employed in producing and controlling chemical reactions which lead to the desired product belong to the chemist, and here he ought to be supreme. In some of the old-established operations an engineer with an elementary knowledge of chemistry may carry on for a time, but in these days a chemist with the most extensive and intimate knowledge of physical chemistry is necessary if these processes are to continue to be profitable. As to the production of dyes and other organic synthetical products the operations involved are in many cases so nearly similar to laboratory processes that the chemist requires very little assistance from the engineer.

As to capital, it is necessary to remember that it will have to be provided liberally. A single fact mentioned in Brunck's lecture on indigo, given already fourteen years ago, shows the spirit in which the German manufacturers attacked the problem of the industrial production of this one colouring matter. They had then invested about £900,000 for this purpose.

I will now describe very briefly a modern chemical works. The lantern pictures exhibited show a general view of the works of Schimmel and Co., at Miltitz, near Leipzig, first occupied in 1901. The works cover about 62 acres. The head office is built over cellars of nearly 22,000 square feet, used as a store for the products of manufacture which,

in this case, consist of essential oils and perfumes. The offices are provided with every kind of modern convenience, together with a printing department furnished with electrically-driven machinery. The main building (24,000 square feet) is occupied by stills and other machinery, and in addition there are several laboratories for special manufacturing operations. A feature to which special attention should be drawn is the research laboratory, a separate edifice providing accommodation originally for fifteen chemists, though since enlarged, and containing a library of several thousand volumes, and a museum. The rest of the area occupied by the firm affords space for a number of villas for the resident portion of the staff, and cottages for workpeople. The whole is surrounded by extensive fields in which roses are cultivated.

The works of the Badische Anilin u. Soda Fabrik, at Ludwigshafen, are arranged on a different plan, because their products are so diversified; but the same principle is recognised, namely, the inseparability of research and manufacture. A number of rectangular buildings, four stories high, are so arranged that the railway lines may traverse the works in two directions at right angles to each other. Each building is devoted to the production of one substance or closely allied group of substances. The top floor is occupied by the laboratory of the chief chemist attached to that department with several assistants. Below is found an intermediate floor where processes previously tested in the laboratory, or suggested as the result of research, may be tried on a scale sufficiently large to determine their practicability before being transferred to the lower floors where the actual manufacture is conducted. I doubt if anything so complete or so commercially successful exists elsewhere in the world.

How many chemical manufacturers among us can boast that they regard science in a light so serious as to have provided in their works a properly equipped laboratory with a competent staff whose occupation is not confined to the analytical testing of materials or products, but extends to the systematic endeavour to introduce improvements into old methods or the discovery of new ones? A few such enlightened firms do exist, but the figures quoted show how much mischief has already been done.

A variety of other questions have recently been raised in view of the circumstances which have been forced on our notice by the war. There is not time for the discussion of the state of the law as to patents, but a couple of sentences in Schimmel's report for April, 1908, show that "great alarm has been caused in the wholesale chemical industry of Germany by the new British Patent Act, which came into force on January 1, 1908, according to which every patent may be declared void if it is exclusively exercised abroad without sufficient grounds. Many firms are thereby compelled to transfer a part of their production to the United Kingdom, a fact which, in the interests of many thousands of German workmen, is sincerely to be regretted."

With regard to duty free alcohol, I am informed, on the best authority, that the regulations in this country are now comparable with those of the German Government, and that there is very little ground for complaint. In the vast majority of cases suitably denatured alcohol can be employed without loss or inconvenience.

There has been a good deal of discussion on the subject of trade marks and proprietary names, much of which I regard as futile. With regard to drugs there should be no great difficulty in instructing the medical profession in those comparatively few cases in which the names are changed.

In conclusion, two remarks only require to be made. The establishment of what will be practically a new industry in this country will require consideration and assistance from the State, if it is to survive the period of fierce competition which will follow the conclusion of the war. Encouragement is already promised to the dye industry, in the form of definite financial aid to be given

by Government. But remembering that the colour maker is dependent on the production of many chemicals, which represent intermediate stages in the processes which lead from the raw materials to the finished product, and that the production of these chemicals is naturally associated with other chemical manufactures, it is to be hoped that the temporary protection will be extended beyond the immediate field of the colour maker.

The other remark may raise a smile on the part of those business men who are moved only by commercial considerations. There will be a great temptation when the war is over to resume former business relations with the enemy. The German chemical manufacturers have a powerful organisation and many years of experience behind them. Let them keep any markets they can retain outside the British Empire, but every man who cares for his country will surely demand that business at home shall be limited to British goods.

THE RED THORN.

By EUCLID C. MARSTON.

THE specimen belongs to the genus *Crataegus*, the different species of which are so difficult to distinguish. The ripe fruit was gathered from a thorn patch near Lisbon, Iowa, from shrubs about 15 feet in height. It is common from the North-Eastern United States to the Dakotas, and as far south as Missouri. The colour of the fruit is a deep red, each from 0.7 to 1 cc. in diameter. The fruit is woody, and could not be ground in mortar and pestle. It could with difficulty be cut with a knife. On burning the fruit gave off a disagreeable odour, like that of burning leaves.

The Sugars.

We placed 200 grms. of the dried fruit in a litre flask fitted with an inverted condenser and treated with alcohol. The solution was removed each day, and a fresh portion of alcohol added. The first extractions were of a dark brown colour, but they afterwards changed to amber. After removing the alcohol by distillation, a thick dark brown solution remained, with an odour of sugar. At the end of fifteen days a test with Fehling's solution showed only a trace of sugar. Water was substituted for alcohol, and continued for twenty-five days longer. The water extraction was almost black, and on evaporation gave out an odour of boiling syrup. The extractions were concentrated, and the sugar determined with Fehling's solution. The sugar content was found to be 35.37 per cent of the dried fruit.

The sugar solution was treated for some hours with bone-black on the hot-water bath, but even after repeated additions of the charcoal the solution remained quite dark. The osazone test with phenylhydrazine and sodium acetate indicated glucose and fructose.

The Oils.

After the extraction of the sugars, the residues were thoroughly dried in an oven at 110°. They were finely ground and the oils extracted with ether in a 500 cc. flask fitted with an inverted condenser. Every second day the ether was poured off, distilled, and a fresh supply added. This was continued for about five weeks, when all the oil was removed. It was of a light yellow colour. It was purified by digesting with ether and bone-black. Only 1.5243 grms. were obtained, or 0.76 per cent of the original fruit—an amount too small for satisfactory tests. A saponification by the Koetstorfer method was completed in twelve hours. The experiment indicated that the oil is laurin.

The Ash.

Several different portions of the berries, of 3 grms. each, were ashed in a platinum evaporating dish and the various constituents determined as follows:—

	Per cent.
SiO ₂	1.36
Al ₂ O ₃	10.78
Fe ₂ O ₃	0.00
MgO	4.77
CaO	15.18
K ₂ O	27.65
Na ₂ O	28.17
SO ₃	2.07
P ₂ O ₅	10.91
Total	100.89

The ash was 3.18 per cent of the original fruit.

The Proteins.

A few of the berries were boiled a few minutes in distilled water. Nitric acid was added, and a yellow colour resulted, which turned to orange on making alkaline, indicating albumen. A portion was boiled after adding a solution of lead acetate and sodium hydroxide until the precipitate dissolved. The colour became very dark, indicating the presence of sulphur.

The nitrogen was determined from 3 grms. of the fruit by the Kjeldahl-Gunning method. We obtained 0.55 per cent nitrogen.

Acids.

Portions of the sugar solution were tested for acids, and tartaric, citric, and acetic acids were found, the last probably from the fermentation of the sugar.

Many thanks are due to Dr. N. Knight for helpful suggestions.

Cornell College, November 11, 1914.

RADIUM.*

(Concluded from p. 302).

APPENDIX I. (continued).

THE price of radium appears for some time to have been holding steady at about 120 dols. per milligram. of radium metal. This does not mean that the material is bought in the elementary condition but that the radium chloride and radium bromide, which are on the market, are paid for on the basis of the metallic radium they contain. This method of payment is a distinct advance over the old method of paying the same price indiscriminately for the chloride or bromide. This price of 120 dols. per milligram. of the metal is equivalent to approximately 91,000 dols. per gram. of radium chloride (RaCl₂), or 70,000 dols. per gram. of anhydrous radium bromide (RaBr₂). Whether this price will rise, fall, or remain stationary can not be predicted. There is no question that there is to be an increased radium production and that meso-thorium is also coming upon the markets in increasing quantity, but the uses of and demand for radium are apparently developing at an even greater rate. Furthermore, the supply of the material is limited and no large resources are in sight. Only one estimate has been published of the total quantity of radium in the Colorado carnotite deposits and that was 900 grms. This estimate is at least five times as large as has been made by any employee of the Bureau of Mines, reckoning all known deposits in the whole American field, even including material too low grade to be marketable. Besides the radium, the uranium and the vanadium present in carnotite are available assets, and recent developments indicate that all the uranium produced will soon be readily sold, while it is well known that there is a ready market for vanadium for vanadium steel.

The value to the public of these deposits is, however, not to be measured in dollars and cents. The value of

* Report No. 214, presented to the House of Representatives, U.S.A., at the 63rd Congress.

the radium output of America will never compare with that of several of our common metals. The total value of the radium in the world's output of radium ores in 1912 was little more than 1,000,000 dols. Accordingly the value must ever be reckoned in what it can accomplish for the public knowledge and the public weal. No certain prediction can be made of the ultimate value of radium or of its possible applications to science or medicine, but enough has been done to show that radium is worthy of the fullest investigation by our highest scientific and medical authorities. Developments in its application to medicine are coming fast. The foreign medical press contains many apparently authentic reports of cures by its use. Interesting developments are also under way in America, and those who have had the largest personal experience in its use are most enthusiastic over its future application. The public may soon look to important publications from leading American authorities who have had real experience in radium therapy. It is to be greatly regretted that owing to the high price of the material, only three or four American surgeons have, so far as the Bureau of Mines is informed, been able to use it in quantities sufficient for the drawing of decisive conclusions. In the progress of the future applications of radium to the curing of disease, nothing is more to be feared than its use in nostrums of every kind. The "wonders of radium" have been so extensively exploited in the public press that already the name is being employed as a psychological agent in advertisements of all kinds of materials, many of which contain no radium at all or, if this element is indeed present, in such small quantities that no therapeutic value can be expected. As bearing on the need of further experiment, attention is called to the fact that the concentrated action of large quantities of radium may effect cures that have been impossible with the smaller amounts heretofore available to the medical profession. It is doubtful if there is at the present time in the hands of the medical profession of America more than a single grm. of this rare element, and the results of investigations soon to be published will show that the concentrated action of the gamma rays from several hundred milligrams. arrest certain forms of cancer and other malignant growths when smaller quantities are without beneficial effect. It is highly important that the medical profession should also have some guarantee of the material they purchase even if it is purchased in small quantities, and I am glad to note that the U.S. Bureau of Standards is preparing to standardise radium preparations. As several frauds in the sale of radium have already been perpetrated upon American physicians, they should all require that the quality of the material purchased should be certified under conditions which prevent error.

In closing, I take pleasure in saying that I am authorised by the Director of the Bureau of Mines to announce that a co-operative agreement has been entered into with the newly organised National Radium Institute, whereby the Bureau obtains the opportunity of a scientific and technological study of the mining and concentrating of carnotite ores and of the most efficient methods of obtaining radium, vanadium, and uranium therefrom, with a view to increased efficiency of production and the prevention of waste.

The National Radium Institute was recently incorporated with the following officers:—

Howard A. Kelly, of Baltimore, President.

Curtis F. Burnam, of Baltimore, Vice-President.

Archibald Douglas, of New York, Secretary and Treasurer.

James Douglas, of New York, and E. J. Maloney, of Wilmington, additional Directors.

The Institute has no connection with the mining of pitchblende, details of which recently appeared in the Denver papers. It has, however, obtained the right to mine twenty-seven claims in the Paradox Valley region, among which are some of the best mines in this richest radium-bearing region of the world. Nearly 100 tons of

high-grade carnotite have already been procured. Under the agreement with the Bureau of Mines the technical operations of the mines and mill are to be guided by the scientific staff of the Bureau. Work will begin in an experimental plant to be erected in Colorado, using entirely new methods developed at the Denver office of the Bureau of Mines. Concentration experiments also will be conducted in the Paradox, probably at the Long Park claims, and if successful will be applied to reducing the wastes that now take place. Within a year at most the mill operations should make results certain and the extraction of ore and production of radium will then be continued on a larger scale. The separation of uranium and vanadium will also be studied, a contract having already been signed for all of these by-products that may be produced. All processes, details of apparatus and plant, and general information gained will be published for the benefit of the people.

The Institute is supplied with sufficient funds to carry out its plans. The Institute has been formed for the special purpose of procuring enough radium to conduct extensive experiments in radium therapy with special reference to the curing of cancer. It also expects to carry on investigations regarding the physical characteristics and chemical effects of radium rays, and it hopes, in time, to be able to assist or perhaps even duplicate the effects of these rays by physical means.

Actual experience, especially of the Institute's president, in the application of the 650 milligrams. of radium and 100 milligrams. of meso-thorium already in his possession, has led him and his associates to believe that with larger supplies many of the variables that cannot now be controlled may be fully correlated, and that radium may become the most effective agent for the treatment of cancer and certain other malignant diseases. Important results have already been obtained by using high concentration of the gamma rays of radium with the alpha rays entirely cut off and the beta rays largely eliminated. Hospital facilities in Both Baltimore and New York are already supplied.

The activities of the Institute are sure to be of benefit to the prospector and miner by providing a greater demand for his already rare ore; to the plant operator by developing methods and by creating a larger market for his product; and to the people by assisting, and possibly by succeeding, in controlling the most malignant of diseases. The radium produced is intended for the Institute's own use and will consequently remain at home.

The Bureau of Mines is especially fortunate in this opportunity to co-operate in the technological features of the work of the National Radium Institute.

Bureau of Mines, Washington.

APPENDIX II.

*The National Radium Institute.**

By ARCHIBALD DOUGLAS, Secretary National Radium Institute.

Through the investigations of the United States Bureau of Mines it became evident in the latter months of 1912 that valuable radium ores were being shipped abroad to be manufactured into radium which was being sold back to this country at prices entirely incommensurate with those paid for the ores themselves. But worse than this, it was discovered that at least twice as much uranium oxide and its accompanying radium was being wasted in the low-grade ores that were thrown on the dump and the fine carnotite dust was being swept away by the winds and rain. Knowing the excellent work being accomplished by the Austrian Radium Institute and the Radium Institute of London, Charles L. Parsons, Chief of the Division of Mineral Technology, of the Bureau of Mines, proposed to Dr. Howard A. Kelly, of Baltimore, and Dr. James Douglas, of New York—both of whom he knew to be

* From the *Mining and Scientific Press*, Jan. 5, 1914.

deeply interested in securing radium for use in two hospitals with which they were closely connected—that they form a radium institute and endeavour to work up some of our American ores and keep the radium in this country for use among such of our own people as could be reached by such quantities as were secured.

It was agreed, if the ores could be procured, that the radium institute would be founded and necessary funds furnished to work up the raw material. Mr. Parsons went with Dr. Kelly to the Paradox Valley, in Colorado, and inspected the mines there. On their return a conference was held with the officers of the Crucible Steel Mining and Milling Co., who owned twenty-seven claims, sixteen of which contain carnotite, in Montrose County, Colo., which it had been holding pending such time as it would pay to extract the vanadium and uranium therefrom. The officers of the Crucible Steel Mining and Milling Co., appreciating the immense good that the radium in these ores might accomplish, consented to have these claims worked on a royalty basis under an agreement covering the return of the uranium and vanadium content of the ore to them. Further conferences were then held with Drs. Kelly and Douglas, and the National Radium Institute was incorporated, as announced in the paper given by Mr. Parsons before the American Mining Congress at Philadelphia, October 24.

For some months the Denver office of the Bureau of Mines had been carrying on laboratory experiments and investigations in the field with reference to the uranium ores, and a bulletin covering these investigations has just been published by the bureau. Knowing of the work of the Bureau of Mines, the National Radium Institute proposed a co-operative agreement with the Bureau of Mines whereby the bureau was offered an opportunity for scientific and technologic study of the mining and concentration of the carnotite ores in the claims secured by the National Radium Institute and for studying in the plant of the institute the most efficient methods of obtaining radium, vanadium, and uranium therefrom, with a view to increased efficiency of production and the prevention of waste. The legality of the agreement was carefully looked into and full approval given by the Government officials, it being found that there were many precedents in similar co-operative work, especially between the Department of Agriculture and the farmers of the country.

In the agreement with the Bureau of Mines the technologic management of the mines and mills was to be guided by the scientific staff of the bureau, and Mr. Parsons has been designated by the director to have charge of the investigation. He will be assisted by R. B. Moore, physical chemist in charge of the Denver laboratory, who will have direct management of the plant, and by Karl L. Kithil, mineral technologist of the bureau, who will be in charge of the mining and concentration. Plans have been completed and contracts let for the experimental plant to be erected at Denver, land for the plant has been leased, over 100 tons of carnotite have already been obtained, and the larger part of the apparatus has been ordered.

In connection with the production of radium, the separation of uranium and vanadium will also be studied, and all processes, details of apparatus and plant, and general information gained will be published for the benefit of the people. As a result of these experiments it is hoped that other plants will be erected, and that our carnotite ores will be worked up at home and the radium kept in this country. The Institute was formed for the special purpose of procuring enough radium to conduct extensive experiments in radium therapy, with special reference to the curing of cancer. It is also expected to investigate the physical characteristics and chemical effects of radium rays.

The radium produced will not be for distribution, as the work of Dr. Kelly has distinctly shown that to get real results in the treatment of cancer and other malignant diseases a high concentration of gamma rays is essential,

and this at the present time can only be obtained from a comparatively large amount of material. Accordingly, to distribute the radium among many hospitals or physicians would render it practically ineffective for this purpose. Some hospitals at both New York and Baltimore are already partly supplied, and while it will be some time before a sufficient quantity of radium is produced from these ores to add greatly to the present usefulness of these hospitals, it is sincerely hoped that the work of the Institute will be of real benefit to many by assisting or possibly in controlling cancer, the most malignant of diseases.

Besides being of benefit to the general public, the activities of the Institute are sure to assist the prospector and miner by providing a greater demand for his already rare ore and by assisting to conserve the large waste which is now taking place; also to the plant operator by developing methods and by creating a larger market for his products. The radium produced is intended for the Institute's own use and is not for sale or distribution.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 5, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President,
in the Chair.

THE PRESIDENT referred to the following losses by death sustained by the Society during the vacation:—Joseph Bemrose, Henry Boyers, Jeffrey Hale Burland, Henry Fairrie, Harry Marshall Freear, Edward Riley, Maung San U, William Frederick Keating Stock, Robert Williamson.

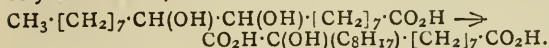
Messrs. L. E. Hinkel and H. W. Cremer were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Hugh Logie Allan, care of The Burma Oil Co., Ltd., Rangoon, Burma; Henry Atlas, 58, High Street, Dartford; William Bacon, B.Sc., Springfield, Springfield Road, New Southgate; Charles Kelway Bamber, The Martyrs, Crawley; Shish Chandra Banerji, Department of Land Records and Agriculture, Cawnpore, U.P., India; Durgasanker Bhattacharje, 3, Sitaram Ghose's Street, Calcutta, India; Arthur Henry Bowell, University College, Auckland, New Zealand; Alexander John Boyd, 64, Newbattle Terrace, Edinburgh; John Bradshaw, M.Sc., Vernon House, Monument Park, Wigan; Frank Brinsley, M.Sc.Tech., Berlin Villa, Stellenbosch, S. Africa; James Mickle Brown, B.Sc., 176, Carter Knowle Road, Sheffield; John Arthur Cresswick, Cress Dale, Villiers Street, Bexley, N.S.W., Australia; Harry Cunliffe, 7, Rinkvale Cottages, Hawick; James Ferguson, Langston, Harpenden, Herts; Alexander Fleck, B.Sc., Hazelbank, Blenheim Avenue, Stepps, Glasgow; George Noel Grinling, 62, Cartwright Gardens, W.C.; Charles Cochrane Iles, M.D., The Hampden Club, Phoenix Street, N.W.; George King, M.Sc., 25, Whitmore Road, Small Heath, Birmingham; Herbert Levinstein, M.Sc., Ph.D., 24, Railway Approach, S.E.; Joseph Frederick Levy, 26, Compton Terrace, Highbury, N.; James Lyttle McKee, B.A., Ph.D., 4, Carrigside, Cork; Alfred Edgar Newland, B.Sc., Government University, Peking, China; Henry Cecil Ratcliffe, 24A, Woodside Road, Bowes Park, N.; Joseph Drummond Robertson, The King's College, Taunton; Rajkumar Sen, M.Sc., 14/3, Manicktola Street, Calcutta, India; William Kershaw Slater, B.Sc., Eastdene, Chamber Road, Shaw, Oldham; Henry Michael Spiers, B.A., B.Sc., Caius College, Cambridge; Alan West Stewart, D.Sc., 29, Westbere Road, West Hampstead, N.W.; Mark Thompson, B.A., Queen's College, Cambridge; Hugh Vivian, 25, Sketty Road, Swansea.

Of the following papers, those marked * were read:—

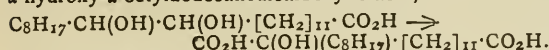
*263. "The Mechanism of the Action of Fused Alkalies. Part I. The Action of Fused Potassium Hydroxide on Dihydroxystearic Acid and Dihydroxybehenic Acid." By HENRY RONDEL LE SUEUR and JOHN CHARLES WITHERS.

The acid $C_{18}H_{34}O_5$ produced by the fusion of dihydroxystearic acid with potassium hydroxide (Le Sueur, *Trans.*, 1901, lxxix., 1313) is now shown to be α -hydroxy- α -octylsebacic acid,—



When α -hydroxy- α -octylsebacic acid is oxidised with potassium permanganate it gives θ -ketomargaric acid, $C_8H_{17} \cdot CO \cdot [CH_2]_7 \cdot CO_2H$, and when it is heated above its melting-point it gives a mixture of the two isomeric acids, $C_8H_{17} \cdot C(CO_2H) \cdot CH \cdot [CH_2]_6 \cdot CO_2H$ and $C_7H_{15} \cdot CH \cdot C(CO_2H) \cdot [CH_2]_7 \cdot CO_2H$. These isomeric acids, on reduction, give α -octylsebacic acid, $CO_2H \cdot CH(C_8H_{17}) \cdot [CH_2]_7 \cdot CO_2H$.

Dihydroxybehenic acid on fusion with potassium hydroxide behaves like dihydroxystearic acid, and gives α -hydroxy- α -octyldodecanedicarboxylic acid,—

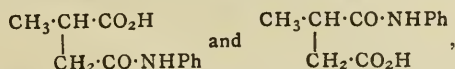


The formation of α -hydroxy- α -octylsebacic acid, and α -hydroxy- α -octyldodecanedicarboxylic acid from dihydroxystearic acid and dihydroxybehenic acid respectively involves the migration of the group C_8H_{17} from one carbon atom to another adjacent to it, and it was pointed out that the migration of such a heavy group is very uncommon, if not hitherto unknown, in the aliphatic series.

*264. "Studies in the Succinic Acid Series. Part II. Anilides and Anilic Acids and the Effect of Steric Hindrance on the Formation of the Amides." By GEORGE FRANCIS MORRELL.

Methods have been worked out to obviate the production of a large proportion of closed-chain products in the preparation of the open-chain neutral aniline derivatives of succinic acid and its methyl derivatives, and thus by improvements on the processes of Menshutkin (*Annalen*, 1872, clxii., 187) and of Tingle and Cram (*Am. Chem. Journ.*, 1907, xxxvii., 597) succin- and methylsuccin-anilides have been obtained in excellent yield.

Of the acid aniline derivatives it was only necessary to investigate methylsuccin-anilic acid, which although theoretically existing in two isomeric forms,—



was hitherto, in spite of all attempts to isolate the two substances by Anschütz, Auwers, Bone, and others, known only as a substance with a melting-point given variously as 143° , 147° , and 149° . From methylsuccinic anhydride, and also methylsuccin-anil, both of the isomerides have been prepared and isolated, the one melting at 159° and the other at 123° . They are particularly sensitive to heat in aqueous solution, being converted into gum-like substances, and this probably accounts for the more soluble of the two acids being previously overlooked.

The preparation of the neutral amides of the succinic acids can only be achieved from the esters by the action of ammonia, and it has been found that the most satisfactory results are obtained by allowing the methyl esters to react with aqueous ammonia in the cold, sufficient alcohol being added to procure solution. The use of alcoholic ammonia in a heated tube gives a much poorer yield (Fischer's method, *Ber.*, 1902, xxxv., 844). Incidentally, cis- and trans-dimethylsuccinamide have been prepared for the first time; they melt and decompose at 244° and 238° respectively. The rate of amide-formation progressively

falls off with the substitution of methyl groups in the succinic acid, and the results suggest that one is here dealing with a case of steric hindrance.

*265. "The Alkaloids of Quebracho Bark. I. The Constitution of Aspidospermine." By ARTHUR JAMES EWINS.

Aspidospermine, $C_{22}H_{30}O_2N_2$, the most abundant alkaloid of *Aspidosperma quebracho* (Quebracho blanco), has been found to contain one methoxyl group and an acetyl group which is attached to a nitrogen atom. It contains no N-methyl group.

When boiled with dilute mineral acids, aspidospermine loses its acetyl group, and a new crystalline base, deacetylaspidospermine, $C_{20}H_{28}ON_2$, is produced. This base on acetylation again yields aspidospermine. Deacetylaspidospermine (m. p. $110-111^\circ$) is an optically active diacidic secondary-tertiary base, which gives a crystalline hydriodide, $C_{20}H_{28}ON_2 \cdot 2HI$ (m. p. 243°), a monobenzoyl derivative (m. p. $186-187^\circ$), and, on treatment with nitrous acid, a nitro-nitroso-derivative (m. p. $155-156^\circ$). With methyl iodide it gives a compound, $C_{20}H_{28}ON_2 \cdot 2CH_3I$.

Aspidospermine, when boiled with concentrated hydriodic acid (D 1.7), gives a base, aspidosine, $C_{19}H_{26}ON_2$, derived from the original alkaloid by simultaneous hydrolysis of the methoxyl group and removal of the acetyl group. It gives a crystalline iodide, $C_{19}H_{26}ON_2 \cdot HI$, melting at above 280° . Both this base and deacetylaspidospermine give intense colour reactions with ferric chloride and with oxidising agents generally.

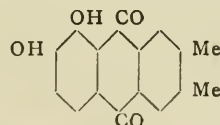
On oxidation with chromic acid, aspidospermine gives a crystalline base (m. p. $192-193^\circ$), which forms a sparingly soluble crystalline hydrochloride (m. p. $286-287^\circ$). To this base the formula $C_{15}H_{24}O_2N_2$ is provisionally assigned.

266. "Some Homologues of Alizarin." By HARRY BRADBURY and CHARLES WEIZMANN.

The authors have studied the condensations of hemipinic anhydride and 4-methoxyphthalic anhydride with o-xylene, and the following substances have been prepared:

Dihydroxy-2-xylylbenzoic acid, isolated from the first condensation, crystallises from acetic acid in small needles melting at 238° . Its constitution is still a matter of doubt.

The above acid leads to the formation of two dimethyl-alizarins, but only the constitution of one of these has been definitely determined. This has been shown to possess the structure—



since it leads to the formation of pyromellitic acid by oxidation with potassium permanganate. This quinone melts at 276° , being more readily soluble in acetic acid than the other quinone melting at 198° , both of which crystallise in yellow needles, and resemble alizarin in properties.

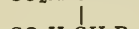
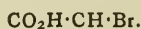
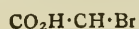
The condensation of 4-methoxyphthalic anhydride with o-xylene is analogous in character to the above-mentioned, but in this case two hydroxy-2-xylylbenzoic acids have been isolated. The acid obtained in greater quantity crystallises from acetic acid in small needles melting at 228° , and gives only one hydroxydimethylantraquinone, which is of a pale green colour, and separates from acetic acid in needles melting at 210° .

The other acid was obtained only in small quantity, being more soluble in benzene than the former, and crystallises from this solvent in needles which melt at 184° .

267. "The Reaction between Benzylamine and the Dibromosuccinic Acids." By EDWARD PERCY FRANKLAND.

The action of benzylamine on s-dibromosuccinic acid (I.) has been shown (*Trans.*, 1911, xcix., 1775) to result

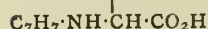
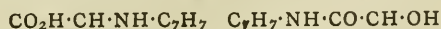
in the formation of a dibenzylaminosuccinic acid and the dibenzylamide of *i*-tartaric acid:—



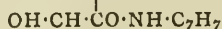
I.

II.

The present investigations show that the isomeric acid (II.) undergoes a similar reaction, yielding an isomeric dibenzylaminosuccinic acid (III.), accompanied by a small quantity of the dibenzylamide of racemic acid (IV.):—



III.



IV.

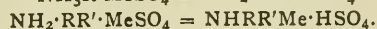
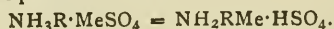
From a comparison of the properties of the two dibenzyl-amino-acids it appears probable that the new acid has the racemic structure, analogous to II., and to the more soluble diaminosuccinic acid which yields racemic acid with nitrous acid, whereas the previously described dibenzylaminosuccinic acid from *s*-dibromosuccinic acid has apparently a "meso" structure analogous to that of *s*-dibromosuccinic acid and the diaminosuccinic acid first obtained by Lehrfeld.

The action of benzylamine on *s*-dibromosuccinic acid has been re-investigated with a view to isolate the products intermediate to the formation of dibenzylaminosuccinic acid, and thereby throwing light on the structural changes which would account for a symmetrical dibenzylamino-acid being derived from a symmetrical dibromosuccinic acid. So far the only intermediate products identified with certainty are benzylamine salts of bromomaleic acid. The isomeric acid (II.) correspondingly yields salts of bromofumaric acid.

268. "The Isomeric Transformation of Ammonium Methyl Sulphate and of Substituted Ammonium Methyl Sulphates. The Interaction of Amines and Methyl Sulphate." By EMIL ALPHONSE WERNER.

In a recent communication on the decomposition by heat of the methyl sulphates of certain isocarbamides evidence was obtained that ammonium methyl sulphate can undergo isomeric change in accordance with the equation $\text{NH}_4\text{MeSO}_4 = \text{NH}_3\text{Me}\cdot\text{HSO}_4$.

The reaction has been examined quantitatively, and a study of the change has been extended to a number of substituted ammonium methyl sulphates, with the result that the property of undergoing isomeric transformation has been found to be common to all those derivatives where an interchange in the position of a hydrogen atom and a methyl group is possible, and may be represented by the general equations:—



In the case of ammonium methyl sulphate and methylammonium methyl sulphate the change proceeded slowly up to 220°, above which it increased rapidly, and was almost complete at 275° after fifteen minutes' heating. With derivatives containing the phenyl group the isomeric change took place readily at much lower temperatures. Neither ammonium ethyl sulphate nor ammonium *n*-propyl sulphate undergoes any isomeric change.

The simple preparation of various substituted ammonium methyl sulphates from the interaction of amines and methyl sulphate takes place strictly in accordance with the equations $\text{NH}_2\text{R} + \text{Me}_2\text{SO}_4 = \text{NH}_2\text{RMe}\cdot\text{MeSO}_4$ and $\text{NHR}_2 + \text{Me}_2\text{SO}_4 = \text{NHR}_2\text{Me}\cdot\text{MeSO}_4$, and contrary to the conclusions arrived at by Ullmann (*Annalen*, 1903, cccxxvii., 104), who obtained mixed products, which, it was pointed out, were no doubt the results of more or less isomeric change dependent on the rise of temperature allowed to take place during the interactions.

A theory of the mechanism of the isomerisation of the ammonium methyl sulphates based on dissociation as a preliminary to the change was suggested.

269. "Carboxylic Acids Derived from cycloButane, cyclopentane, cycloHexane, and cycloHeptane." By LEONARD JAMES GOLDSWORTHY and WILLIAM HENRY PERKIN, jun.

The authors have prepared the *cis*- and *trans*-modifications of cyclobutane-1 : 2 : 3-tricarboxylic acid, and have devised an improved method of preparation of the *cis*- and *trans*-modifications of cyclopentane-1 : 2 : 4-tricarboxylic acid. The *cis*- and *trans*-modifications of cyclohexane-1 : 2 : 4-tricarboxylic acid and the *trans*-modifications of cycloheptane-1 : 2 : 4-tricarboxylic acid were also described.

270. "Resolution of *trans*-cyclopentane-1 : 2-Dicarboxylic Acid." By LEONARD JAMES GOLDSWORTHY and WILLIAM HENRY PERKIN, jun.

The authors have succeeded in resolving *trans*-cyclopentane-1 : 2-dicarboxylic acid by means of brucine. The *d*-acid melts at 181°, and has $\alpha_D + 87.6^\circ$; the *d*-ethyl ester boils at 170°/100 mm., and has $\alpha_D + 70.31^\circ$, and the *d*-anilide melts at 245–247°, and has $\alpha_D + 110.1^\circ$. The *l*-acid melts at 180–181°, and has $\alpha_D - 85.9^\circ$; its *ethyl* ester boils at 170°/100 mm., and has $\alpha_D - 69.76^\circ$.

271. "Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part X. The Optical Dispersive Power of Tetrahydro-2-naphthol and its Esters." By JOSEPH KENYON and ROBERT HOWSON PICKARD.

The optical dispersive power of tetrahydro-2-naphthol is simple under conditions for which that of the *x*-naphthyl-alkylcarbinols is complex. A convenient means of purifying *ac*-tetrahydro-2-naphthol is by the crystallisation from water of the sodium salt of its hydrogen phthalate.

272. "A Simple Demonstration of the Formation of Biuret from the Interaction of Carbamide and Cyanic Acid." By EMIL ALPHONSE WERNER.

The current view, which is freely expressed in the textbooks and works of reference, namely, that biuret is formed from the condensation of two molecular proportions of carbamide with loss of one molecular proportion of ammonia, whilst true in substance, is quite fallacious as an explanation of the mechanism of the change.

It has been suggested by the author (*Trans.*, 1913, ciii., 1014) that the production of biuret originates from the interaction of carbamide and its dissociation product, cyanic acid, in the "keto-form," $\text{HN}\cdot\text{CO}$, a view which has the full support of experimental evidence, since it has been shown that the formation and decomposition of biuret is a truly reversible reaction (*Trans.*, 1913, ciii., 2281).

A further proof in support of the truth of the above theory is supplied by the following simple experiment:—To 3 grms. of carbamide dissolved in 4 cc. of concentrated hydrochloric acid diluted with 2 cc. of water, 4 grms. of powdered potassium cyanate are gradually added with constant stirring; after a short interval the solution (previously filtered to remove some cyanamide which has separated), when tested in the usual manner with copper sulphate and alkali, will be found to give a strong biuret reaction. Considering the very unfavourable conditions in the experiment, since the greater part of the cyanic acid is lost as the result of hydrolysis, polymerisation, and volatilisation, only a small proportion of biuret could be reasonably expected to be formed. An estimation of the biuret produced in a rough experiment of this kind showed that approximately 4 per cent of the theoretical amount, according to the equation $\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{OH} + \text{HNCO} = \text{NH}[\text{C}(\text{NH})\cdot\text{OH}]_2$ (*iso*-biuret or "enol-form"), had actually been formed, and must have resulted as shown above, as no ammonia can have been removed from carbamide under the conditions of the experiment.

The formation of biuret in this way is of theoretical interest, since the reaction is strictly analogous to that by

which substituted iso-biurets have been obtained by Bruce (*Journ. Am. Chem. Soc.*, 1904, xxvi., 449) from the isomeric transformation of certain isocarbamide cyanates.

273. "The Corrosion of Iron and its application to Determine the Relative Strengths of Acids." By JOHN ALBERT NEWTON FRIEND and CHARLES WILLIAM MARSHALL.

Iron readily corrodes when immersed in dilute solutions of the mineral salts of the alkali metals. The corrosion may, however, be inhibited by the addition of sodium carbonate. In general the amounts of carbonate required to produce inhibition bear a close relationship to the relative strengths of the acids of the mineral salts. The quantities of sodium carbonate required to inhibit corrosion in the presence of varying quantities of the same sodium salts have been determined. When the results are shown graphically a distinct resemblance can be traced to the specific conductivity curves of the free acids.

274. "Colorations produced by some Organic Nitro-compounds, with special reference to Tetranitromethane." (Part I.). By ERNEST MAGOWAN HARPER and ALEXANDER KILLEN MACBETH.

A fuller account of the work indicated in a preliminary note (*Proc.*, 1913, xxix., 304) was given.

On mixing substances containing an unsaturated centre or an atom capable of exercising a higher valency with tetranitromethane the colour obtained deepens on keeping. Examination of the absorption spectra shows that they undergo a great change, a strongly selective effect developing with maximum absorption at $1/\lambda$ 2850 approximately.

In the case of the mononitro-compounds the effect is absent save in the case of the alkyl nitrites. Deep colorations are obtained with all those examined when they are subjected to the same conditions as tetranitromethane (see *Proc.*, xxx., 15). An hypothesis was advanced to account for these colorations, and their analogy to those produced by tetranitromethane forms the basis of an hypothesis to account for the latter.

This postulates the isomerisation of one, or more, of the nitro-groups in tetranitromethane to a "nitritic" form. This also occurs in other polynitro-compounds containing more than two nitro-groups attached to the same carbon, or in substances containing two nitro-groups attached to the same carbon and a labile hydrogen atom.

275. "The Absorption Spectra of Sulphurous Acid and Sulphites." By ROBERT WRIGHT.

An examination of the absorption spectra of sulphurous acid and various sulphites and sulphonates points to the conclusion that aqueous sulphurous acid consists to a large extent of uncombined sulphur dioxide molecules. The absorption spectrum of gaseous sulphur dioxide strongly resembles that of the aqueous solution in that both exhibit the same band. The sulphites, on the other hand, show only general absorption.

276. "Rotatory Power and Refractivity. Part I. The Rotatory Powers, Refractivities, and Molecular Solution Volumes of Borneol, Cinchonidine, and Benzoylcinchonine in certain Solvents." By DAVID HENRY PEACOCK.

Hitherto the explanations of the dependence of rotatory power on concentration have assumed a definite modification of the degree of asymmetry of the molecule. Livens (*Phil. Mag.*, 1913, [6], xxv., 817) has shown that, assuming that the variation is solely due to variations in the velocity of light within the solution, $[\alpha]$ should vary as $(n^2 - 1)(n^2 - 1 + 1/\alpha)$, where " α " is a constant and n = refractivity of the solution. For the solutions examined this appears to hold, and therefore the variations in $[\alpha]$ are not due to deformations of the molecule by the internal pressure of the solvent or other causes affecting the degree of asymmetry. Also for one solution it was shown that the variation in molecular solution-volume is probably to be ascribed to the variation in density of the solvent.

PHYSICAL SOCIETY.

Ordinary Meeting, November 27, 1914.

Dr. A. RUSSELL, Vice-President, in the Chair.

A PAPER entitled "Note on the Conduction of Electricity at Point Contacts" was read by Mr. A. F. HALLIMOND.

The paper deals with the "characteristic" or volt-ampere curves given by various "Point" contacts when the voltage is slowly varied. The curves were plotted by means of a form of rocking mirror galvanometer, which projected the characteristic as the path of a spot of light on the screen, the co-ordinates being respectively proportional to the current and voltage.

The first part describes the behaviour of a typical contact, zincite-tellurium. The well-known unilateral curve is terminated by a sudden breakdown of resistance, after which the contact has a more symmetrical characteristic of lower resistance at the origin. By allowing the contact to stand under a certain voltage with zincite positive it may frequently be restored to the condition of high resistance in which it again yields the unilateral curve.

The second part describes the results obtained on examining the characteristics for the forty-five contacts possible between ten chosen substances. The conclusion is reached that the results in all cases are similar to those given by zincite tellurium. No line could be drawn separating "metallic" contacts from those in which one or both conductors were "crystals."

The results obtained are expressed in terms of a series in which the higher member behaves towards the lower as zincite to tellurium.

Series: Zincite, brookite, molybdenite, chromium, galena, inserite, chalcocite, copper, chalcopyrite, tellurium.

In the third part the conclusion is drawn that in a contact yielding the unilateral (high resistance) curve, the resistance lies within the surface of the member standing higher in the series. Rough measurements showed that the weight required in these contacts diminished from about 1000 grms. for zincite to very light contact for the substances lying near tellurium, and it is suggested that this gradation in weight determines the relative positions arrived at for the respective substances.

DISCUSSION.

Mr. DUDELL thought the author's method of obtaining continuous curves much more satisfactory than the ordinary method, as it gave less chance of the point contacts altering during the experiment, and, further, the arrangement of the minerals in the table he gave appeared to have some correspondence with their order of sensibility when used as wireless detectors.

Mr. D. OWEN attributed much of the success of the author's experiments to the attention paid to the preparation of polished surfaces of contact. It would be useful if the author would specify the curvatures employed. The two types of characteristic might be accounted for by the greater or less extent to which the electrostatic attraction between the contacts extend, type B occurring when that effect was large. Calculation proved that, assuming a P.D. of only one volt, and a distance apart of 10^{-7} cm. (ten times the molecular distance), the electrostatic pull was of the order of 1000 grms. *wt./mm²*. It might in some cases be much greater than this.

Mr. P. R. COURSEY thought the chief point of interest in the paper was the table in which the substances were arranged in the order of the effects obtained with them. It would be of considerable use if some connection could be found between this arrangement and some of their physical or chemical properties. He asked if the author had obtained any evidence of a hysteresis effect in the contacts. With reference to the jumping of the characteristic from the "A" to the "B" type of curve by the application of excessive voltage, it seemed evident that this must be what happened when a strong "X" was received, though

he had noticed with a zincite-tellurium detector that the impact of a strong atmospheric often increased the sensitivity of the contact. On one occasion he had obtained a curve with a particular zincite-bornite contact which was concave to the volt axis on the side with zincite positive, but convex with zincite negative. He had failed to obtain this with other samples of the same minerals.

Prof. FORTESCUE communicated the following:—The curves given in Fig. 1 are very interesting. I have repeatedly noticed the same thing with the zincite and galena series of contacts. The breakdown is apparently due to increase of area of the contact, brought about by the increase of mechanical pressure or by the softening, or even fusing, of one of the materials when high voltages are applied. The restoring effect of the reverse current is not so easy to explain; possibly it may be some electrolytic action. I have never found a point which had been rendered conductive by heavy mechanical pressure restored in this way. The tabulation of the substances given on page 2 can also be carried out from their thermo-electric properties with similar results. Carborundum, however, presents a difficulty, as it can be strongly positive or negative, and is to a large extent independent of the mechanical power.

The AUTHOR, in reply, thought it likely that some connection would exist between the table and the behaviour of the contacts as detectors. He had not been able to connect this series with one derived from other physical properties. He had noticed hysteresis as described by Pierce, but assigned it to alteration and recovery. The action of an "X" on the detector could scarcely be predicted from the change in the characteristic alone. If the "X" were strongly damped the first impulse might tend either to breakdown or recovery. The curvature of the surfaces appeared to be immaterial, and no special shape beyond that of a blunt point was attempted. He did not think the electrostatic attraction offered, of itself, any possibility of a unilateral effect since the force on interchanging + and - signs would be the same. Some other unilateral property would still be required. The recovery of the contact was undoubtedly one of the most difficult features of these curves. It seemed impossible to conceive a mechanical change which would be reversible to such an extent. He felt that the published thermo-electric data which he had encountered were too sparse and too conflicting to permit a comparison with any degree of certainty.

A paper on the "Thermal Conductivity of Badly Conducting Solids" was read by Mr. T. BARRATT.

The thermal conductivities of several typical solids of low thermal conductivity have been determined by the same method, and, in the main, the same apparatus, as was recently employed by the author for pure metals and alloys. The substances tested include electrical insulators, such as glass, fused silica and ebonite, various kinds of wood, and some partial conductors of electricity, viz., carbon and graphite.

In a former paper it was shown that the thermal conductivity k is given by—

$$k = \frac{H^2 \coth^2 al}{\rho q h V^2},$$

or, where " l " is sufficiently great,—

$$k = \frac{H^2}{\rho q h V^2},$$

where H is the heat given to one end of the specimen, of length l , perimeter p , and cross-sectional area q ; V is the difference of temperature of the "hot" end of the specimen and the enclosure; h is the heat lost from 1 sq. cm. of the surface per second when its temperature is $t^\circ \text{C}$. above that of the enclosure; and—

$$a = \sqrt{\frac{hp}{qk}}.$$

In nearly every case the simpler form of the equation could be used.

For the first time in the measurement of thermal conductivity a direct comparison of this quantity in the case of a non-metal has been made with that of a metal—viz., bismuth—whose conductivity is of the same order of magnitude as those of some of the non-metals.

The results agree well with those obtained by Prof. Lees' "disc" method in cases where direct comparison is available.

DISCUSSION.

Dr. HARKER mentioned that the formula used by the author assumed that the isothermal surfaces in the specimen were plane. This would not be far wrong in the case of good conductors, but it might introduce serious error in the case of substances such as those now treated. He also doubted the validity of the assumption that " h " was proportional to V for any but very small differences of temperature. The results given in the paper for firebrick were about twenty times lower than those given by other observers, including recent determinations of his own.

Mr. F. E. SMITH asked why the second platinum thermometer was not put inside the water jacket. He was not sure that it was justifiable to assume that the end of the rod that fits in the copper cylinder is at the temperature given by the platinum thermometer P_{t_1} . Was the end of the copper plug blackened in the same way as the specimen rods? He did not like the symbols used by the author, which were not those generally employed.

Dr. RUSSELL said that it was important to know how much of the heat was lost by radiation and how much by convection currents. The author's emissivity constant seemed to include both. With ordinary copper wires suspended in air it was known that about 90 per cent of the total heat emitted was taken away by convection currents, and only about 10 per cent was lost by radiation. Newton showed that the convected heat carried away was proportional to the difference of temperature between the cooling body and the surrounding medium, and hence, so far as the convection loss was concerned, the author's assumption was justified. Stefan's law applied to the radiation loss, and, strictly speaking, the assumption that this loss was proportional to the difference of temperature was only permissible for small differences of temperature. Luckily, however, this loss was small, and he did not think that the accuracy of the results obtained was appreciably affected by the assumption.

The AUTHOR communicated the following reply:—The points raised by Dr. Harker are, I believe, in each case due either to misapprehension or to misprints in the advance proofs. In the first place, the diameters of the specimens were 5 to 6 millimetres (not centimetres, as given in one part of the paper). The ratio of the sectional area to the thermal conductivity thus remains approximately the same as in the experiments on metals. This part of the criticism applies to practically all recent determinations of the thermal conductivity of metals where the dimensions of specimens are of the same order as in the present experiments. As Dr. Russell remarks, Newton's law of cooling is applicable to that part of the heat lost by convection, and also very nearly to that lost by radiation, provided the excess of temperature of the rod is not great. In the present research this excess of temperature was no greater than 10.6°C . Finally, the value of " k " in the case of firebrick is that given in the main table of results—viz., 0.0010. The value referred to by Dr. Harker is again a misprint. In reply to Mr. Smith, it is not safe to have a bare platinum thermometer in water or steam, and, in addition, the temperature to be measured (P_{t_2}) is that of the actual enclosure. In answer to the next point, I consider it quite justifiable to assume that the temperature of the "hot" end of the cylinder was the same as that of the rest of the copper cylinder containing the thermometer P_{t_1} , as the enclosing cylinder was of thermal capacity greatly in excess of that of the specimen rods. The end of the "copper plug" was blackened

in precisely the same way as the rods. Dr. Russell's remarks as to the probable ratio of convection to radiation are interesting, and I hope shortly to determine this ratio in the case of my own arrangement of apparatus.

SOCIETY OF CHEMICAL INDUSTRY.
(LONDON SECTION).

Ordinary Meeting, December 7, 1914.

Dr. W. R. HODGKINSON in the Chair.

The following papers were read and discussed :—

"Reduction of Antimony and Bismuth Oxides by their Sulphides." By W. R. SCHOELLER, Ph.D.

The author states that antimony sulphide and trioxide, fused together in a current of inert gas, yield metal and sulphur dioxide. The reaction becomes rapid at about 900° C., but it is never complete on account of the volatilisation of both sulphide and oxide in the gas current; the highest yield of sulphur dioxide was 50 per cent of the theoretical. If antimony sulphide and trioxide be fused in a crucible under a layer of salt, they react with formation of antimony-glass, no metal being liberated. Bismuth oxide and sulphide, says the author, easily interact at low temperatures, giving metal and sulphur dioxide, at the same time a small quantity of basic bismuth sulphate is formed.

"The Removal of Carbon Bisulphide from Coal Gas." By E. V. EVANS, F.I.C., F.C.S.

The sulphur compounds remaining in coal gas after the removal of sulphuretted hydrogen consist mainly of carbon bisulphide, and the proportion by volume of this constituent in the gas is about 0.02 per cent. Owing to this state of extreme dilution only reactions of high chemical velocity are suitable for the removal of this impurity on a large scale. An investigation into the known reactions of carbon bisulphide led to the conclusion that its decomposition by heat possessed the greatest possibilities of technical application.

Carbon bisulphide is not appreciably decomposed into its elements at 500° C. in the presence of nitrogen, but with hydrogen (or coal gas containing hydrogen), as the gaseous carrier, the velocity of decomposition is greatly accelerated, and proceeds according to the equation, $CS_2 + 2H_2 = 2H_2S + C$. The carbon deposited on the heated contact or catalytic material is removed by a process of combustion *in situ*, whilst the sulphuretted hydrogen produced is absorbed by oxide of iron. The rate of decomposition of carbon bisulphide is a function of (1) temperature, (2) surface of heated material exposed to the gas, (3) the type of catalyst chosen. For the application of the reaction to a large scale a temperature of 450° C. was selected as the intrinsic quality of the gas was not impaired, and iron vessels for containing the catalyst could be suitably employed at this temperature. Iron turnings were first used as catalyst, but difficulties arose owing to the high temperatures attained when attempting to aerate the material for the removal of the deposited carbon. By impregnating a porous body with the catalyst, and thus separating the metallic particles, intense local chemical action during aeration was presented, and this process became manageable. A more active catalyst had to be employed owing to the extra contact required when depositing the catalyst on a porous nucleus, and this was found in nickel reduced from the chloride. Several unsuccessful attempts were made to reproduce the laboratory conditions and results on a large scale, and the author deals briefly with the salient points which eventually led to the erection of a plant capable of purifying 15 million cubic feet per day at the East Greenwich Works of the South Metropolitan Gas Company. By this process about 80 per cent of the sulphur compounds of gas are converted to sulphuretted hydrogen, the remaining sulphur consisting

mainly of thiophene. Ammonia is produced in small quantity due to the hydrolysis of hydrocyanic acid. The oxygen of the gas is almost completely removed, though the volume of gas before and after treatment remains unaltered. The methane content of the gas is slightly increased. The presence of sulphuretted hydrogen in gas before treatment decreases the efficiency of this process, which cannot therefore be advantageously applied to crude coal gas. It is found that carbon oxysulphide is produced by conducting gas containing carbon monoxide and sulphuretted hydrogen over the heated catalyst, the following reactions taking place :—



Both reactions are reversible, and the formation of carbon oxysulphide only becomes appreciable when the quantity of sulphuretted hydrogen in the gas exceeds 100 grains per 100 cubic feet. The capital outlay for plant is £1500 per unit for dealing with one million cubic feet of gas per day, whilst the working costs entailed in operating the process represent 0.03d. per 1000 cubic feet; the latter includes interest on capital, depreciation, repair, and maintenance.

SOCIETY OF PUBLIC ANALYSTS AND
OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, December 2, 1914.

Mr. A. CHASTON CHAPMAN, President, in the chair.

MESSRS. John Kent Crow and Horace Finnemore were elected Members of the Society.

A certificate was read for the first time in favour of Mr. David Mitchell, Oakhouse, Grafton Place, Euston Square, N.W.

Certificates were read for the second time in favour of Messrs. Harold Stanley Machin and Frederick Robinson.

The following papers were read :—

"Application of Spectrography to Analytical and Industrial Chemistry." By S. JUDD-LEWIS.

After a brief review of spectroscopy generally, the photography of visible and ultra-violet spectra by the quartz spectrograph is described, and details of the procedure for obtaining arc and spark spectra are given. Interpretation by means of, and on the principles of, comparison spectra receive special attention. Several instances of the application of spectrography to the technical study of waters, minerals, metals, &c. are cited.

"Some Oleaginous Seeds and Fruits." By R. R. BOLTON and ENID M. JESSON.

The authors give analytical data for twelve of the lesser known oleaginous seeds and fruits, describing their botanical and general characteristics as well as those of the oils they yield.

"Corrections in Bomb Calorimetry." By G. NEVILL HUNTLY.

A discussion of the magnitude of the corrections for the fuse, cooling, sulphuric and nitric acids formed, change in the water equivalent with temperature, loss by evaporation, heat developed by the stirrer, and losses due to incomplete combustion. A form is given for reducing the time required for the complete cooling correction and a shortened form of the latter indicated.

"Estimation of Sulphur in Rubber." By R. GAUNT.

Sulphur may be estimated in rubber by burning in dry oxygen and passing the products of combustion through hydrogen peroxide, the sulphuric acid formed being estimated either gravimetrically or volumetrically. The paper describes a simple way of carrying out the process which enables the whole operation to be completed in one and a-half hours.

NOTICES OF BOOKS.

A Text-book of Chemistry. By WILLIAM A. NOYES.
London: G. Bell and Sons, Ltd.

THIS book is intended for the use of college students who are beginning the study of chemistry. The author has reviewed the whole field of inorganic chemistry, and has aimed at the greatest possible simplicity of statement. He begins with a short discussion of the atomic theory and the laws of chemical combination, and passes thence to the study of the elements in the order usually adopted in the older style of text-book. A large amount of detailed information is given in the book, but, on the other hand, some of the explanations are too much curtailed. For example, the definition and discussion of oxidation and reduction is defective and inadequate, and the classification of oxides is dismissed without any explanation of the scientific principles underlying it. Some of the diagrams given are also rather trivial and might well be excluded.

CORRESPONDENCE.

A GERMAN DEBT TO BRITAIN.

To the Editor of the Chemical News.

SIR,—The pre-eminence that Germany has gained in Chemical Industry, and which we shall surely wrest from her if we go about it the right way, should not blind us to facts of an opposite character that tell in our favour.

Dr. Ormanby recently read a paper, "On Britain and Germany in relation to the Chemical Trade," before the Royal Society of Arts, wherein he is reported to have said that it became necessary for Germany "to develop economic methods for the utilisation of the great deposits of low-grade phosphatic iron ores which were those chiefly available," from which statement one would gather that she had "worked out her own salvation."

As a matter of fact Germany owes everything to England in being able to work up her phosphatic ores for modern requirements in steel and iron.

The brilliant invention of Sidney Gilchrist Thomas, the modest police-court clerk, developed as it was by the aid of his cousin (Percy C. Gilchrist) and other helpers, is wholly English; and its history, besides forming an entrancing romance of modern science, may well at the present moment encourage us in the efforts to regain the position lost by us through crass neglect and short-sighted cupidity.

The case is especially encouraging, for here was every reason for the much-praised German chemists to find a means of utilising the vast deposits of their country, and yet an unknown Londoner, the son of a Welsh resident, made the discovery that has brought millions into her treasury during peace and placed her in time of war in the formidable position we but too clearly see.

The early experience of Thomas fits in but too well with Sir William Ramsay's estimate of the German character, for we are told "In Germany there was a short but severe contest with a powerful combination of North German steel manufacturers. These gentlemen attempted to work the process regardless of patent rights, and fought the inventor in the law courts, partly on technical legal grounds, partly on other pretexts." On Nov. 22, 1879, Thomas was, however, able to write from Berlin, "Beaten the enemy on his own ground" (Burnie's "Memoir of Thomas," p. 134), showing that the spirit of fair play was not yet dead in that country.

It would be unjust not to mention the very different treatment meted out to him in Vienna, where a presentation was made to Thomas on behalf of the Prague Iron-works Company, "as a mark of their appreciation of his genius, as well as to express, though in a somewhat

feeble manner, their gratitude for the benefits conferred upon their district by the basic process" (*op. cit.*, p. 173).

The genius of Thomas was specially inclined to the solution of unsolved chemical problems. He used to say, "Impossible as with present lights it may seem, why should not ammonia be extracted from the air?" Had he not been cut off in his prime who shall deny that this further discovery might have benefited the agricultural interests which he laid under obligation with the basic slag from the converting process, and of which Germany took such early advantage as to acquire a monopoly of the product that extended to our own Cleveland—the very coast selected for to-day's shameful raid!

Thomas died barely thirty-five years old, but not before laying Germany under a debt to Britain that her lately revealed intentions have ill repaid.—I am, &c.,

F. J. R. CARULLA.

December 16, 1914.

MISCELLANEOUS.

Water Softeners.—The gratifying increase of activity in many of the manufacturing industries during the past three months is well exemplified by the large number of orders now being placed in this country for water softeners and purifiers, feed-water heaters, &c.,—a sure index of works extensions on a large scale. We are informed that, since the outbreak of war, Messrs. United Water Softeners Limited, the well-known makers of "Lassen-Hjort" and "Permutit" water softening and purifying plants, have entered into contracts to erect over one hundred installations, totalling several millions of gallons daily, for firms in the United Kingdom. Prominent among those who have placed orders for softening plants are the Admiralty (30,000 gallons per day), Vickers, Ltd. (14,000), Armstrong, Whitworth, and Co., Brunner, Mond, and Co. (500,000), The *Daily Chronicle* Paper Mills (240,000), Bickershaw Collieries—Ackers, Whitley, and Co. (360,000), The North Eastern Railway Co. (96,000), British Portland Cement Manufacturers (12,000), Merryweather and Co. (8,000), Curtiss and Harvey (19,000), Sir Joseph Lyons and Co. (24,000), Erith Oil Works (192,000), &c. The considerable extent to which such labour-saving and waste-eliminating appliances are adopted in this country is in itself a refutation of the oft-repeated assertion that British manufacturers are backward in utilising scientific methods of economy in their works processes.

Presents and Parcels for the Troops.—With reference to the letter on this subject which appeared in the *CHEMICAL NEWS* for October 2nd last, Messrs. Neale, Wilkinson, and Co. beg to intimate that they will be unable to accept packages for forwarding to the British Expeditionary Force after December 23. During the three months which have elapsed since they made their offer, they have received and forwarded a vast number of packages, and they are informed that all packages received in France up to December 5 had been duly despatched to their respective consignees. The transport arrangements having been much simplified, Neale and Wilkinson, Ltd. feel there is no longer any need for them to continue their offer. Packages can now be forwarded by Parcels Post up to 7 lbs. weight, and packages above that weight can be sent through the Military Forwarding Officer, Southampton. Packages forwarded to the Military Forwarding Officer, Southampton, must be sent carriage paid to that port, in accordance with the regulations issued by the Press Bureau, copy of which may be obtained from the War Office, Whitehall, S.W.

MEETINGS FOR THE WEEK.

TUESDAY, Dec. 29th. } Royal Institution, 3. (Christmas Lectures,
THURSDAY, " 31st. } adapted to a juvenile auditory). "Science
SATURDAY, Jan. 2nd. } in the Home," by Prof. C. V. Boys, F.R.S.

INDEX.

- ABDERHALDEN, E., and E. Eichwald**, synthesis of optically active halogen hydrines, 108
Aberdeen University, 143
Abonoenc, M., influence of tellurium upon the sensitiveness of selenium to light, 162
Aberystwyth, University College of Wales, 135
Absorption of light, quantitative measurements of, 255
Acetate solutions and acetic acid, effect of dilution on hydrogen potentials of, 292
Acid, acetic, and sodium acetate, hydrogen potentials of mixtures of, 291 and standard acetate solutions, effect of dilution on hydrogen potentials of, 292
benzoic, catalytic decomposition, 186
butyric, catalysis by thorium, 233
camphenic, and its isomerides, 70
chrysophanic, reactions of, 16
dihydroxybenzoic, and dihydroxybenzoic acid, action of fused potassium hydroxide on, 313
hydrochloric, action of cold concentrated, on starch and maltose, 269
solutions, new method for precise standardisation, 194
velocity of nycrolysis of starch and maltose by cold concentrated and fuming, 269
hydrocyanic, new method for determination, 158
isopimaric, products of extreme alkylation of, 279
nitric, and sulphides of β -naphthol, interaction, 83
orthonitroparatoxyacetic, 279
para-chlorophenylselenious, 303
paratoxyacetic, 279
phosphoric, separation of titanium from, with the aid of ammonium salt of nitrosophenylhydroxylamine, 5
succinic, series, studies in, 313
sulphurous, absorption spectra, 315
reaction of p -benzoquinone with, 292
trans-cyclopentane-1:2-dicarboxylic, resolution of, 314
tricarballic, transformation of oxalacetic lactone into, 186
Acids, application of corrosion of iron to determine relative strengths of, 315
acyclic γ -halogen, 60
amino, influence of acids and alkalis on optical activity of, 267
Acids, carboxylic, derived from cyclobutane, cyclopentane, cyclohexane, and cycloheptane, 314
dibasic, acid salts of, 12
dibromosuccinic, and benzylamine, reaction between, 313
diphenyl-2:3:2':3'- and 3:4:3':4'-tetracarboxylic, 293
indene dicarboxylic, and hydriodic acid, 306
 γ -ketonic, new method of preparing, 173
nitric, and nitrous, in rainfall near Melbourne, influence of weather conditions on, 17
organic, preparation and properties of ammonium salts of, 212, 224
Acree, S. F., and J. H. Schroder. (See Schroder, J. H.)
Adiabatic and isothermal compressibilities of liquids between one and two atmospheres' pressure, 231
Adrenalin and carbon dioxide, antagonistic action on the heart, 267
Agricultural yield, analyses of, 266
Air and methane, limits of inflammability of mixtures of, 204
propagation of flame in mixtures of, 294
velocities of flame in mixtures of, 267
ozoneation, 237, 252, 263
sulphur dioxide in, determination of minute amounts of, 17
Alchemical Society, 174, 282
presidential address, 197
Alcohol, application of α -bromonaphthalene to determination of water in moist, 70
electromotive forces in, 280, 293
Alcoholic solutions, dropping electrode in, 293
Aldehydes, synthesis by zinc organo-metallic derivatives, 233
Alloxanes, constitution of N-methyl ethers of, 69
Aliphatic ethylenic compounds, hydrogenation under ordinary pressure in presence of nickel, 198
nitro compounds, theories of formation of, 267
substances, volumetric determination of carbon in, in wet way, 279
Alizirin, homologues of, 313
a methyl ether, 83
Alkali, reaction of p -benzoquinone with, 292
Alkalies, mechanism of action of fused, 313
Alkali-alkyl sulphates and alkali nitrites, interaction, 267
Alkali cyanides, new method for determination, 155
Alkaloid, a new, 31
Alkaloids of Quercus bark, 313
Alkylcyclopentanones obtained by hydrogenation of unsaturated derivatives, 107
Allylcyclohexanones and methylallylcyclohexanones, 119, 162
Aloy, J., and C. Kabaot, characterisation of morphine and phenols by uranium salts, 233
Aluminium and iron, separation of zirconium from, with aid of ammonium salt of nitrosophenylhydroxylamine, 153
nickeling of, 198
separation of titanium from, with the aid of ammonium salt of nitrosophenylhydroxylamine, 5
Alunite as a source of potash salts, 231
Amadori, M., phenomena of transformation of molybdates and tungstates, 174
of sodium molybdate and tungstate, 120
American Chemical Society, 132
Amines and methyl sulphate, interaction, 314
Aminocamphor, derivatives, 69
Ammonium salts of organic acids, preparation and properties, 212, 224
hyurate, migration of methoxy group in decomposition of a quaternary, by Holmann's method, 60
methyl sulphate and substituted ammonium methyl sulphates, isomeric transformation, 314
molybdate, 172
quinone derivatives, 279
Amyloses, plurality of, 222
Analysis, chemical, by secondary Röntgen rays, 8
Analyst, public, work of, in relation to manufactured products, 257
Analytical operations, symbolical representation of, 247
Anderson, V. G., influence of weather conditions upon the amounts of nitric acid and of nitrous acid in rainfall near Melbourne, 127
Andrews, E. R., and J. H. Coste. (See Coste, J. H.)
L. W., new method for the precise standardisation of hydrochloric acid solutions, 194
Animal, a prehistoric, 9
Animals, marine, and fish as sources of oils, 198
of vertical migrations, 8
Anthesis nobilis, constituents of flowers of, 82
Anthocyanins and anthocyanidins, production, 266
Antimony oxide, reduction by its sulphide, 317
Apparatus, glass, supply of, 174
Arc, investigations on, as a generator of high-frequency oscillations, 35
luminous vapours distilled from, 254
Argon, capillary constants for liquid, 303
Arsenic, fixation by the brain after intravenous injections of salvarsan, 266
Arylidenedimethylpyrones and their salts, 71
co-solution, 82
Aspergillus oryzae, enzymes of, and application of its amylolytic enzyme to fermentation industry, 215
Aspidospermine, constitution, 313
Atomic weight of lead, 8, 94, 128
of mercury, 293
of nickel, 12
of silver, 39
of uranium, 162
Atomic weights, annual report of international committee, 255
Atoms, migration of para-halogen, in phenols, 267
question of association, 25
theory of compressible, 22
Australian and Tasmanian eucalyptus, correlation between specific characters of, 126
ores, extraction of radium from, 126
Austrian trade, competition with, 233, 24
Azo compounds, colour and constitution, 70
Azomethines derived from phenylisoxazolone, 198
BADGLEY, Col. F. W., "Gravitation and Aether Waves" (review), 132
Bailey, E. M., some reactions of chrysophanic acid, 16
Bailland J., registration of time signals, 9
Bain, D. W. H. Perkin, jun., and R. Robinson, some derivatives of isocoumarin and isocoumarin, 230
Bainbridge, E. G., experiments on conversion of certain dibromides of type of ethylene dibromide into corresponding glycols, 280

- Baker, H. B., and W. H. Watson, atomic weight of mercury, 29
- R. T., and H. G. Smith, correlation between the specific characters of Tasmanian and Australian eucalypts, 126
- Balbiano, L., dehydration of glycolol, 222
- tribenzoin, 132
- Ball, F., Society of Chemical Industry, 55
- Balls, W. L., and F. S. Holton, analyses of agricultural yield, 266
- Bangor, University College of North Wales, 136
- Barbaliin, transformation into β -barbaloin, 119
- Barbier, P., and R. Locquin, constitution of linalol, 60
- Barbieri, G. A., palladous salicylate, 195
- poly sulphides of calcium, 246
- position of cerium in the periodic table, and the complex molybdates of tervalent cerium, 174
- Baunebey, O. L., detection of cyanides in the presence of ferro- and ferricyanides and thiocyanates, 274
- Barosma, venusta, volatile oil from leaves of, 294
- Bariat, T., thermal and electrical conductivities of rarer metals and alloys, 35
- conductivity of badly conducting solids, 316
- Bases, diagnosis of primary, secondary, and tertiary, 96
- Bassett, H., jun., and H. S. Taylor, calcium nitrite, 71
- H. L., "Elements of Chemistry" (review), 48
- Bataillon, M., stage of activation of phenomenon of parthenogenesis, 23
- Bateson, W., address to British Association, 85, 97, 161
- Battersea Polytechnic, 147, 210
- Bauer, E., action of isocyanide on 1,5-diketones, 96
- M., and A. Brochet. (See Brochet, A.)
- Bausor, H. W., "Chemical Calculations" (review), 36
- Beauzy, M., and P. Delbet. (See Delbet, P.)
- Beet sugar, capturing German trade, 209
- Beetroot culture, 108
- Béhal, A., analysis of essential oils, 120
- Belfast Municipal Technical Institute, 148
- Queen's University, 145
- Belgium, war on German trade in, 306
- Belot, E., primitive oceans and continents, 46
- Bender, A. W., determination of mercuric iodide in tablets, 194
- Benzaldehyde derivatives, absorption spectra of vapours and solutions of, 292
- Benzene and its homologues, bromination, 108
- freezing-point as a fixed point in thermometry, 187
- nucleus, constitution, 1
- Benzoylchloride, rotatory power, refractivity, and molecular solution volume of, 315
- Benzylphenylacetylene dibromide, stereoisomeric forms of, 96
- Benzylamine and dibromosuccinic acids, reaction between, 313
- Benzylsulphonyl derivatives of α -aminoazo compounds, 303
- Berger, E., oxidation of copper, 48
- reduction by hydrogen of nickel and copper oxides in presence of an oxidizing agent, 107
- Bernthsen, A., "Kurzes Lehrbuch der Organischen Chemie" (review), 12
- Berthelot, D., new effects of the ultra-violet rays, 8
- Bertrand, G., and R. Sazerac, favorable action of manganese in acetic fermentation, 198
- Binary mixtures, relations between constitution and thermic properties, 12
- Birkbeck College, 147
- Birmingham University, 137
- Birse, W. M., and F. W. Gray. (See Gray, F. W.)
- Bismuth, organo derivatives of, 279
- oxide, reduction by its sulphide, 317
- Bismuthines, preparation and properties of tertiary aromatic, and their halogen derivatives, 279
- Bissel, D. W., and C. James (See James, C.)
- Biuret, formation from interaction of carbamide and cyanic acid, 314
- Blackburn Municipal Technical College, 143
- Blaise, E. B., hydroxylamine derivatives of 1,4-diketones and N-xy-2,5 dimethylpyrrol, 96
- synthesis of aldehydes by zinc organo-metallic derivatives, 233
- of monochloroketones by zinc organo-metallic derivatives, 233
- Bloch, L., phosphorescence of sulphur, 24
- Blood pressure, effects of fatigue on, 9
- quantitative gravimetric analysis of urea in, 198
- Boiling-points in homologous series, 152, 165
- Bolton, E. K., and E. M. Jesson, some oleaginous seeds and fruits, 317
- Bomb calorimetry, corrections in, 317
- Bonnet, G., scientific jubilee, 23
- Books, Reviews and Notices of—
- "Aether Waves, Gravitation and," 132
- "Agricultural Research Association, Report, 1913," 60
- "Alcoholic Fermentation," 119
- "Analysis, Organic, Methods of Quantitative," 257
- "Animals, Relative Effects of Carbon Monoxide on Small," 197
- "Atoms, Radio-active, Molecular Structure of" (It.), 11
- "Bacon, Roger, Essays by Various Writers," 84
- "Berzelius, Jac., Letters of" (Fr.), 11
- "Boyle, Robert, A Biography," 48
- "British Industry and the War," 282
- "British Pharmacopœia, 1914," 31, 306
- "Calcium Carbide, Storage of Petroleum Spirit and," 160
- "Carbon Compounds, Kinetic Stereochemistry of" (Ger.), 36
- "Carbon Monoxide, Relative Effects on Small Animals," 197
- "Chemical Annual, Van Nostrand's," 257
- "Chemical Calculations," 36
- "Chemical Engineering," 257
- "Chemistry, Elementary Household," 107
- "Chemistry, Elements of," 48
- "Chemistry, First Book of," 185
- "Chemistry, Organic, Introduction to the Study of," 160
- "Chemistry, Organic, Short Text-book of" (Ger.), 12
- "Chemistry, Physiological, Text-book of," 282
- "Chemistry, Technical, Encyclopedia of" (Ger.), 11, 95
- Books, Reviews and Notices of—
- "Chemistry, Text-book of," 318
- "Cirencester, Royal Agricultural Society, Annual Report," 222
- "Clay and Pottery Industries," 160
- "Coal Mines, Gases found in," 246
- "Commerce, the Magnet of," 282
- "Dairy Chemistry," 246
- "Directory, Electrician Electrical Trades, and Handbook for 1915," 282
- "Distillery Questions" (Ger.), 48
- "Electric Furnace, Production of Temperature Uniformity in," 81
- "Electric Furnaces for Making Iron and Steel," 161
- "Electrical Blast-furnace, Heat Balance for Albert Hirth's," 107
- "Electrical Conductivity and Ionisation Constants of Organic Compounds," 305
- "Electrical Trades' Directory and Handbook for 1915," 282
- "Ethylsulphates of the Metals of the Rare Earths, Isomorphism of, &c.," 132
- "Explosives, Lectures on," 60
- "Filters and Filter Presses for the Separation of Liquids and Solids," 246
- "Fire-damp Indicator or Methanometer, Report," 208
- "Fire-Damps, Rare Gases in" (Fr.), 119
- "Foods, Water, Sewage, and other Substances, Chemical Examination of," 306
- "Fuel; Gaseous, Liquid, and Solid, Examination and Thermal Value of," 161
- "Gas Analysis, Technical," 305
- "Gas Chemists' Summary, 1913," 48
- "Gases Found in Coal Mines," 246
- "Gases, Inflammable, in Mine Air," 10
- "Gases, Mine, and Natural Gas, Sampling and Examination of," 10
- "Geology, Introduction to," 281
- "Gravitation and Aether Waves," 132
- "Hirth's Electrical Blast-furnace, Heat Balance for," 107
- "Hydrogen, Preparation and Commercial Uses of," 119
- "Institute of Chemistry of Great Britain and Ireland, History of, 1877-1914," 258
- "Ions, Complex, in Aqueous Solutions," 208
- "Julian, Henry Forbes. Memorials of," 161
- "Leather, the Making of," 131
- "Livingstone College Year Book," 95
- "Magnetic Rays in Different Gases and Gaseous Mixtures, Experimental Researches of" (It.), 12
- "Manchester, Municipal School of Technology, Prospectus of University Courses," 208
- "Matriculation Directory, London," 282
- "Matter, Theory of the States of" (Ger.), 11
- "Metallurgy of the Non-ferrous Metals," 160
- "Metallurgy, Physical, Introduction to the Study of," 306
- "Metallurgy, Principles of," 197
- "Museums, Public Utility of," 132
- "Nitrogen, Fixation of Atmospheric," 59
- "Nitrogen, Industry of Atmospheric" (Fr.), 11
- Books, Reviews and Notices of—
- "Organic Compounds, Identification of" (Ger.), 84
- "Osmotic Pressure of Aqueous Solutions," 161
- "Paper Makers' Directory of All Nations," 208
- "Peroxides and Persalts, Inorganic" (Ger.), 11
- "Petroleum and its Substitutes, Chemistry of," 63
- "Petroleum and Natural Gas in Wyoming, Utilisation," 132
- "Petroleum Spirit and Carbide of Calcium, Storage of," 160
- "Pharmacopœia, British, 1914," 31, 306
- "Philippine Islands, Annual Report of the Bureau of Science," 36
- "Philippine Journal of Science," 234
- "Potash, Topographical Feature of Desert Basins of the United States with reference to Possible Occurrence of," 132
- "Radiation and the Quantum Theory, Report on," 208
- "Radio-active Substances Analysis of, by Sublimation" (Ger.), 11
- "Radio-elements and the Periodic System" (Ger.), 107
- "Roberts-Austen, Sir William Chandler, a Record of His Work," 185
- "Sanitary Engineering," 10
- "Sewage, Water, Foods, and other Substances, Chemical Examination of," 306
- "Stones, Precious" (Fr.), 84
- "Technology, Chemical, and Analysis of Oils, Fats, and Waxes," 281
- "United States National Museum, Report on the Progress and Condition of for the Year ending June 30 1913," 258
- "Van Nostrand's Chemical Annual, 1913," 257
- "Water, Sewage, Foods, and other Substances, Chemical Examination of," 306
- "Winds, the Rose of the," 208
- "Woburn Experimental Station, Report on Field and Pot culture Experiments, 1913," 222
- "Wyoming, Utilisation of Petroleum and Natural Gas in," 132
- "X-Rays," 36
- Boon, A. A., K. J. McKenzie, and J. Trotter, some arylidenedimethylpyrones and their salts, 71
- F. J. Wilson, and I. M. Heilbron, constitution of arylidenedimethylpyrones and their salts, 82
- Borneol, rotatory power, refractivity, and molecular solution volume of, 315
- Boron, amorphous, and magnesium bromide, 293
- nitride, band spectrum of, 286
- Borough Polytechnic Institute, 147
- Bottomley, W. B., some accessory factors in plant growth and nutrition, 10
- Bougault, J., dioxotriazines, 162, 282
- indene dicarbonic and hydridene dicarbonic acids, 306
- saponification of ether salts and amides by concentrated sulphuric acid, 27
- Bourget, H., H. Buisson, and C. Fabry, Nebula Orion, 63

- Boyd, D. R., and E. R. Marie, velocities of combination of sodium derivatives of phenols with olefine oxides, 69
- Bradbury, H., and C. Weizmann, some homologues of alizarin, 313
- R. H., colloids and crystals, the two worlds of matter, 78
- W. A., new form of intermittent syphon, 163
- and F. Owen, estimation of sulphur in motor spirits, 163
- Bradford, City of, Technical College, 138
- Bradshaw, L., H. B. Dixon, and C. Campbell. (See Dixon, H. B.)
- Brady, O. L., isomerism of the oximes, 69
- and F. P. Dunn, isomerism of the oximes, 292
- Brain, fixation of arsenic by, after intravenous injections of salvarsan, 266
- Brass and bronze analysis, rapid quantitative, 183, 189
- Bridge for measurement of self-induction, 269
- Bridgman, J. A., and G. E. F. Lundell. (See Lundell G. E. F.)
- Briner, E., and A. Kuhne, decomposition of calcium carbide, 208
- Bristol, Merchant Venturers' Technical College, 137
- University, 136
- British Association, 108
- Presidential Address, 85, 97, 161
- Chemical Section, Presidential Address, 103, 109
- Engineering Section, Presidential Address, 121
- Mathematical and Physical Science Section, Presidential Address, 91
- Brochet, A., catalytic hydrogenation of liquids at moderate temperature and pressure, 12
- and M. Bauer, hydrogenation of compounds containing ethylenic bonds in presence of nickel, 174
- and A. Cabaret, hydrogenation under ordinary pressure of aliphatic ethylenic compounds in presence of nickel, 198
- Brock, F. P., L. V. Redman, and A. J. Weith. (See Redman, L. V.)
- Bromination of benzene and its homologues, 108
- of cobalt and nickel in presence of ethyl oxide, 162
- of substituted toluene, 268
- Bromine, action on hydroxides of lanthanum and the didymiums, 49
- oxidations with, under influence of light, 174
- solutions, in water, nitrobenzene, and carbon tetrachloride, 294
- hydrate, 186
- α -Bromonaphthalene, its physical properties and application to determination of water in moist alcohol, 70
- α -Bromopentenes, ethylenic isomerism of, 96
- Bronze and brass analysis, rapid quantitative, 183, 189
- Brown, E. W., Royal Medal, 291
- J. C., "Essays and Addresses" (review), 216
- Browne, A. J. J., obituary, 283
- Browning, H., jun., and F. B. Power. (See Power, F. B.)
- P. E., action of bromine on hydroxides of lanthanum and the didymiums, 49
- Brubaker, H. W., some natural indicators, 181
- Bruce, Sir D., Maj. A. E. Hamerton, Capt. D. P. Watson, and Lady Bruce, trypanosome causing disease in man in Nyasaland, 32
- Bühler, F. A., "Filters and Filter Presses for the Separation of Liquids and Solids" (review), 246
- Buisson, H., H. Bourget, and C. Fabry. (See Bourget, H.)
- Burch, G. J., obituary, 287
- Burgess, M. J., and R. V. Wheeler, limits of inflammability of mixtures of methane and air, 294
- propagation of flame in limit mixtures of methane, oxygen, and nitrogen, 294
- Burke, B., melting-point of cane-sugar, 47
- Burrell, G. A., and F. M. Seibert, gas analysis by fractional distillation at low temperatures, 214
- "Gases Found in Coal Mines" (review), 246
- "Inflammable Gases in Mine Air" (review), 20
- "Sampling and Examination of Mine Gases and Natural Gas" (review), 10
- F. M. Seibert, and J. W. Robertson, "Relative Effects of Carbon Monoxide on Small Animals" (review), 197
- Burrows, G. J., inversion of cane-sugar by acids in water-alcohol solutions, 126
- CABARET, A., and A. Brochet. (See Brochet, A.)
- Cadmium in zinc, determination, 250
- salicylate, 198
- Calcium salts, determination of magnesium in, 155
- carbide, decomposition, 208
- carbonate, pure, 150
- cyanamide, solubility in water of nitrate compounds of, 84
- nitrate—lime—water, three component system, 71
- polysulphides, 246
- Calorimetry, bomb, corrections in, 317
- Calvert, W. R., "Utilisation of Petroleum and Natural Gas in Wyoming" (review), 132
- Cambridge Scientific Instrument Co., Ltd., 197
- University, 133
- Campbell, A., and D. W. Dye, measurement of alternating electric currents of high frequency, 32
- C., H. B. Dixon, and L. Bradshaw. (See Dixon, H. B.)
- H. B. Dixon, and W. E. Slater. (See Dixon, H. B.)
- F. H., new method for determination of vapour-pressures, 127
- Camphane series, studies in, 69
- Camphorquinone, isomeric hydrazones of, 69
- Canac, J., and E. Tassilly, nickeling of aluminium, 198
- Canada's gift, 174
- Caoutchouc solutions, osmotic pressure and physical constitution of, 269
- Carajura and Chica red, 83
- Carbinols, normal esters of, of formula $C_2H_5 \cdot CH(OH) \cdot R$, 280
- Carbon and phosphorus, 210
- in aliphatic substances, volumetric determination in wet way, 279
- optical activity of compounds without, 210
- bisulphide, removal from coal gas, 317
- dioxide and adrenalin, autogonistic action on the heart, 267
- monoxide, capillary constants for liquid, 303
- reduction by hydrogen induced by radium emanation, 119
- tetrachloride, solutions of bromine in, 294
- Carbonylferrocyanides, hydrates of, heats of formation, 48
- Cardiff, University College of South Wales and Monmouthshire, 136
- Carnotites, radium: uranium ratio in, 218, 228, 239
- Carulla, F. J. R., a German debt to Britain, 318
- Prof. Bateson's Address to the British Association, 161
- Sir William Crookes and Sir Henry Roscoe as educationalists, 95
- was it prophetic? 222
- Caspari, W. A., osmotic pressure and physical constitution of caoutchouc solutions, 269
- Catalysis, 279
- studies in, 267
- Cellulose, chemical constitution, 45
- hemipermeability to the ions, 81
- Cellulose, methylation of, 292
- Cerium, complex molybdates of, 174
- position in periodic table, 174
- Cerusi, Prof., the sun is a star of the magnitude -26.5, 47
- Challenger, F., organo derivatives of bismuth, 279
- and C. K. Tinkler. (See Tinkler, C. K.)
- Chantard, J., origin of petrols, 30
- Chapin, R. M., practical method for the preparation of dry starch, soluble in cold water, for use as an indicator, 195
- Chapman, A. C., nitrogenous constituents of hops, 68
- Chavanne, G., ethylenic isomerism of α -bromonaphthalene, 96
- Chelsea, South Western Polytechnic Institute, 148
- Chemical Society, 68, 82, 255, 267, 278, 291, 302, 313
- industries, capture of Germany's, 151
- qualification, professional, 146
- Chemicals, supply to Britain and her dependencies, 295, 308
- Chemists and the gas mantle shortage, 176
- Chemistry, analytical and industrial, application of spectrography to, 317
- Applied, Ninth International Congress, 108
- Chevenard, M. P., nickel steels, 24
- Chicoré and Carajura, 83
- Chlorine and gaseous nitric oxide, rate of combination, 83
- Chlorocamphor, a new, 70
- Chlorometric method, Penot's, 174
- Choline ethers, 119
- Chree, C., the 27-day period in magnetic phenomena, 32
- Christmas cards, 264
- Chromium in iron and steel, determination, 207
- Cinchonine, rotatory power, refractivity, and molecular solution volume of, 315
- Cinematograph in research, 14
- Cirencester, Royal Agricultural College, 138
- Ciusa, R., and A. Piergallini, oxidations with bromine under the action of light, 174
- Clack, B. W., coefficient of diffusion in dilute solutions, 270
- Clarena, J., Penot's chlorometric method, 174
- Clarke, H. T., "Introduction to the Study of Organic Chemistry" (review), 160
- Rosalind, and A. Senier. (See Senier, A.)
- Clausmann, P., and A. Gautier. (See Gautier, A.)
- Clematis vitalba, constituents of, 82
- Clerkenwell, Northern Polytechnic Institute, 148
- Clewer, H. W. B., and F. Tutin. (See Tutin, F.)
- Coal, composition of, 293
- in Madagascar, 24
- solvents of, 119
- Coates, J. E., and Ada Finney, rate of combination of gaseous nitric oxide and chlorine, 83
- Cobalt, bromination in presence of ethyl oxide, 162
- Coefficient of diffusion in dilute solutions, 270
- Cohen, J. B., position-isomerism and optical activity, 267
- and C. J. Smithells, chlorination and bromination of substituted toluene, 268
- Coker, E. G., address to Engineering Section of British Association, 121
- Colloids, 43, 83
- and crystals, the two worlds of matter, 78
- Colorations produced by organic nitro-compounds, with special reference to tetranitromethane, 315
- Colour-using industries, effect of the war on, 254
- Colouring matters contained as glucoside in flowers of some Indian plants, 69
- of Rhamnus catharticus, 281
- Comandon, Dr., life of the infantesimal, 23
- Combustion, regularity between molecular heat of, and its bearing on constitution of the hydrocarbons, 26, 37
- Conduction of electricity at point contacts, 315
- Conductivities, thermal and electrical, of rarer metals and alloys, 35
- Conductivity, thermal, of badly conducting solids, 316
- Constants, capillary, for liquid carbon monoxide and liquid argon, 303
- Continents and oceans, primitive, 46
- Cooke, J. H., and G. T. Morgan. (See Morgan, G. T.)
- Cooper, W., determination of cadmium in zinc, 250
- W. F., and W. H. Nuttall, condensation of furan-2:5-dialdehyde with malonic ester and malonic acid, 278
- Cooper-Key, Major A., "The Storage of Petroleum Spirit and Carbide of Calcium" (review), 160
- Copper, oxidation of, 48
- and reduction of, 108
- sources of the world's supplies in 1913, 253
- oxide, catalytic action on combination of oxygen and hydrogen, 162
- reduction, 173
- by hydrogen in presence of a dehydrating agent, 107
- Cork, University College, 145
- Corburet, R., allyl and methylallylcyclohexanones, 162
- allylcyclohexanones and methylallylcyclohexanones, 119
- and A. Haller. (See Haller, A.)
- Cornwall, School of Metaliferous Mining, 148
- Coste, J. H., and E. R. Andrews, "Examination and Thermal Value of Fuel—Gaseous, Liquid, and Solid" (review), 161
- Cotton, spacing experiments with Egyptian, 266
- Courtois G., glycolate and lactate of uranyl and some uranyl salts of polyacid of fatty series, 96
- organic uranium salts, 48
- Cousin and Volmar, M.M., nitro and amino derivatives of orthocyanophenol, 198
- Cox, A. J., "Annual Report of the Bureau of Science, Philippine Islands" (review), 36
- M. W., and T. W. Richards. (See Richards, T. W.)
- Crofts, J. M., and H. B. Dixon. (See Dixon, H. B.)

- Crommelin, C. A., capillary constants for liquid carbon monoxide and liquid argon, 303
- Crookes, Sir W., acquired radioactivity, 254
- Address to the Royal Society, 287
- to the Society of Chemical Industry, 56
- and Sir Henry Roscoe as educationalists, 93
- spectrum of elementary silicon, 31, 113
- Crossley, A. W., "Preparation and Commercial Uses of Hydrogen" (review), 119
- Crystal twinning and the martensitic structure, 299
- Crystals and colloids, the two worlds of matter, 78
- Crystalline form, chemical significance of, 50, 63
- Cullis, H. E., and B. Lambert. (See Lambert, B.)
- Curie, M., differences in atomic weight of lead obtained from different minerals, 94
- Curtis, W. E., wave-lengths of hydrogen lines and determination of the series constant, 33
- Cyanamide industry, present state of, 20, 28
- Cyanides, detection in presence of ferro- and ferricyanides and thiocyanates, 274
- Cyclopentadiene and its dimers, derivatives of, 107
- DAISH, A. J., action of cold concentrated hydrochloric acid on starch and maltose, 269
- velocity of hydrolysis of starch and maltose by cold concentrated and fuming hydrochloric acid, 269
- Daniels, F. C. T., determination of chromium and manganese in iron and steel, 207
- Darspsky, A., "Kurzes Lehrbuch der Organischen Chemie" (review), 12
- D'Altoff, A. T., "L'Industrie de l'Azote Atmosphérique" (review), 11
- De Broglie, M., chemical analysis by secondary Röntgen rays, 8
- De Coninck, O., cadmium salicylate, 168
- and M. Gérard, determination of atomic weight of nickel, 12
- De Forcrand, R., preparation of hydrates of manganese sulphate, 107
- thermo-chemical study of hydrates of manganese sulphate, 160
- De Lange, M., thermophone, a new form of telephone, 302
- De Lavisson, M. R., foundation of new prize of physiology, 23
- De Rohden, C., presence of rare earths in Scheelite, 197
- Delbet, P., and M. Beaudy, ultra-violet rays and sursums, 31
- Delépine, M., optical decomposition of iridotrioxalates, 186
- Denham, W. S., and Hilda Woodhouse, methylation of cellulose, 292
- Deperet, Prof., a prehistoric animal, 9
- Desch, C. H., crystal twinning and the martensitic structure, 299
- hardness of solid solutions, 297
- Dialkylacetophenones, action of epihalohydrines on, 12
- Dibromides of the type of ethylene dibromide, conversion into corresponding glycols, 280
- 2:3-Dibromonaphthalene, 71
- Didymium, action of bromine on hydroxides of lanthanum and the, 49
- Diffusion, coefficient of, in dilute solutions, 270
- Diketo-5:6-dimethoxyhydrindene, 287
- 1:4-Diketones, hydroxylamine derivatives of, 96
- 1:5-Diketones, action of sodamide on, 96
- γ -Diketones, acetylenic, syntheses of, 12
- Dilution law, 304
- Dimethylallylacetophenone and its oxidation products, 162
- 6:6'-Dimethylindigotin, 279
- Dinaphthathioxonium salts, 83
- Dioximines, chemical constitution, 268
- Dioxytriazines, 162, 282
- Diphenylnitrosamine, action of acids on, in hydroalcoholic solution, 48
- Dixon, H. B., L. Bradshaw, and C. Campbell, firing of gases by adiabatic compression, 268
- C. Campbell, and W. E. Slater, photographic analysis of explosion-flames traversing a magnetic field, 10
- and J. M. Crofts, firing of gases by adiabatic compression, 268
- Dohson, G., atmospheric electricity observations made at Kew Observatory, 35
- Dodgson, J. W., reaction of *p*-benzoquinone with sulphurous acid and with alkali, 292
- Dole, R. B., hypothetical combinations in water analysis, 169
- Douglas, A., National Radium Institute, 311
- Drury, A. N., validity of the microchemical test for the oxygen place in tissues, 9
- Dublin University, 133
- Ducelliez, F., L. Gay, and A. Raynaud. (See Gay, L.)
- and A. Raynaud, bromination of cobalt and nickel in presence of ethyl oxide, 162
- Duff, J. C., *p*-toluylacetic acid, *o*-nitro-*p*-toluylacetic acid, and 6:6'-dimethylindigotin, 279
- Dufraisse, C., stereoisomeric forms of bromide of benzoyl-phenylacetylene, 96
- Dundee, University College, 143
- Dunn, F. P., and O. L. Brady. (See Brady, O. L.)
- Dupont, G., synthesis of acetylenic γ -diketones, 12
- Durham University, 140
- Dye, D. W., and A. Campbell. (See Campbell, A.)
- EARTH, levelling of, 31
- Earths, rare, in scheelite, 197
- East Ham Technical College, 148
- Eastick, J. J., "Filters and Filter Presses for the Separation of Liquids and Solids" (review), 246
- Edinburgh, Heriot-Watt College, 144
- University, 144
- Eichwald, E., and E. Abderhalden. (See Abderhalden, E.)
- Electric current, a perpetual, 23
- currents of high frequency, measurement of alternating, 32
- Electricity, atmospheric, observations made at Kew Observatory, 35
- conduction at point contacts, 315
- Electrode, dropping, in alcoholic solutions, 293
- Electrodes, combinations of the hydrogen and calomel, 280
- Electronic orbits, approximately permanent, and the origin of spectral series, 286
- Elliott, J. C., and G. T. Morgan. (See Morgan, G. T.)
- Ellipsoidal bodies, potential of, and figures of equilibrium of rotating liquid masses, 32
- Enzymes of *Aspergillus oryzae* and application of its amylolytic enzyme to fermentation industry, 215
- Epihalohydrines, action on dialkylacetophenones, oxypropylenedimethylacetophenone, and derivatives, 12
- Equilibrium figures of rotating liquid masses and potential of ellipsoidal bodies, 32
- Escard, J., "Les Pierres Précieuses" (review), 84
- Espil, L., and P. Sabatier. (See Sabatier, P.)
- Esters of carbinols of formula $C_2H_5 \cdot CH(OH) \cdot R$, 280
- Ether, oxalacetic, preparation of derivatives of α -pyrone from, 162
- salts and amides, saponification by concentrated sulphuric acid, 27
- Ethers in essential oils, determination, 233
- of choline, 119
- Ethylene bonds, hydrogenation of compounds containing, in presence of nickel, 174
- Ethyl hydrindine-2:2-dicarboxylate, reduction products, 293
- Eucalypts, Tasmanian and Australian, correlation between specific characters of, 126
- Euston, E., nature of basic lead carbonate, 13
- Evans, E. V., removal of carbon bisulphide from coal gas, 317
- Everest, A. E., production of anthocyanins and anthocyanidins, 266
- Ewins, A. J., alkaloids of Quebracho bark, 313
- Explosion-flames traversing a magnetic field, photographic analysis of, 10
- Explosives, was it prophetic? 222
- FABRY, C., H. Bourget, and H. Buisson. (See Bourget, H.)
- Fajans, K., "Die Radio-elemente und das Periodische System" (review), 107
- Faraday Society, 246
- Feeder, mechanical liquid, 199
- Fegely, W. H., R. E. Lee, and J. P. Trickey. (See Lee, R. E.)
- Fenestre, Cadisch, and Co., pure calcium carbonate, 150
- Ferguson, J., the mirror of alchemy, 197
- Fermentation, favourable action of manganese in acetic, 198
- industry, application of amylolytic enzyme of *Aspergillus oryzae* to, 215
- Ferments, accustoming to toxic substances, 8
- Ferrous and cupric salts, compounds of nitric oxide with, 84
- Fever, evolution of the spirilla of recurrent, 8, 23
- Fildes, P., and J. McIntosh. (See McIntosh, J.)
- Finney, Ada, and J. E. Coates. (See Coates, J. E.)
- Fish, a rare, 68
- and marine animals as a source of oils, 198
- Fiske, A. H., and T. W. Richards. (See Richards, T. W.)
- Flame, propagation in limit mixtures of methane, oxygen, and nitrogen, 294
- in mixtures of methane and air, 294
- velocities of, in mixtures of methane and air, 267
- Fleming, J. A., atmospheric refraction and its bearing on the transmission of electromagnetic waves round the earth's surface, 34
- Flour, bleached and unbleached, 245
- Flowers of *Anthemis nobilis*, constituents, 82
- of *Matricaria chamomilla*, constituents, 291
- Fluorine in potable waters, 233
- Flüßscheim, B., constitution of the benzene nucleus, 1
- Folly and Sergeant, MM. (See Sergeant, M.)
- Forces, electromotive, in alcohol, 280, 293
- Forster, M. O., and E. Kunz, studies in the camphane series, 69
- R. B., and A. Seier. (See Seier, A.)
- Fosse, R., A. Robyn, and F. Francoir, quantitative gravimetric analysis of the urea in blood, 198
- Foster, Mr., radium, 264, 276, 284, 301, 310
- Foulds, R. P., and R. Robinson, some derivatives of safole, 267
- Fournéau, E., and H. J. Page, ethers of choline, 119
- Frank, C. E., colloids, 83
- Francoir, R. Fosse, and A. Robyn. (See Fosse, R.)
- Frankland, E. P., reaction between benzylamine and the dibromosuccinic acids, 313
- Franklin, M. W., air ozonation, 237, 252, 263
- Free, E. E., "Topographic Features of the Desert Basins of the United States with reference to the Possible Occurrence of Potash" (review), 132
- French Association for the Advancement of Science, 81
- Friend, J. A. N., and C. W. Marshall, corrosion of iron and its application to determine relative strengths of acids, 315
- Fruits, oleaginous, 317
- Fuel, oil, water in, rapid methods of estimating, 245
- Furan-2:5-dialdehyde, condensation with malonic ester and malonic acid, 278
- Furness, R., R. T. Hardman, and E. Newbery, electromotive forces in alcohol, 280
- GALVANISED products, tests for, 132
- Galway, University College, 146
- Garcia, C. A., liberation of nitrogen in reaction of NaOBr on urea, 117
- Gardiner, C. J., "Introduction to Geology" (review), 281
- Gas, action of radium emanation upon detonating, 210
- analyses by fractional distillation at low temperatures, 2, 14
- coal, removal of carbon bisulphide from, 317
- synthetic preparation, 198
- electrolytic, ignition-points of mixtures containing, 263
- mantle shortage, 176
- pressure regulator, 305
- reactions, ionisation produced by, 33
- Gases, firing by adiabatic compression, 263
- ideal reactivities of, 70
- rare, attempts to produce by electric discharge, 31
- retained by silver, 179
- Gaskell, W. H., obituary, 288
- Gault, H., oxalocitric lactone and its transformation into tri-carballic acid, 186
- preparation of derivatives of α -pyrone from oxalacetic ether, 162
- Gaunt, R., estimation of sulphur in rubber, 317
- Gautier, A., address to French Association for the Advancement of Science, 81
- and P. Clausmann, fluorine in potable waters, 233

- Gay, L., F. Ducliez, and A. Raynaud, bromination of benzene and its homologues, 108
- Gelin, M., A. Kling, and M. Laseur. (See Kling, A.)
- Geological survey of the United States, 24
- Gérard, M., and O. De Coninck. (See De Coninck, O.)
- German and Austrian trade, report of emergency committee on competition with, 244
- and Austro-Hungarian trade, competition with, 233
- chemical trade, 107
- debt to Britain, 318
- trade, capturing, beet sugar, 209
- displacing, 258
- in Belgium, war on, 306
- Germany's chemical industries, capture of, 151
- Germann, F. E. E., and P. A. Guey. (See Guey, P. A.)
- Ghose, B., and S. Smiles, dipnathathioxonium salts, 83
- Gibbs, I. R., and P. W. Robertson, experiments on the migration of para-halogen atoms in phenols, 267
- Gill, Sir D., obituary, 287
- Giran, H., bromine hydrate, 186
- Girard, P., hemipermeability of the cellulose to the ions, 81
- Giraud, M. J., coal in Madagascar, 24
- Glasgow, Royal Technical College, 144
- Glucinum sulphate and its hydrates, 173
- Glycoll, dehydration of, 222
- Glycols, conversion of dibromides of the type of ethylene dibromide into, 280
- β*-Gnoscopine, synthesis of, 279
- Godchaux, L., war on German trade in Belgium, 306
- Godchot, M., thujone and thujamenthone, 108
- Goldsworthy, L. J., and W. H. Perkin, jun., carboxylic acids from cyclobutane, cyclopentane, cyclohexane, and cycloheptane, 314
- resolution of trans-cyclopentane-1:2-dicarboxylic acid, 314
- Gooch, F. A., F. C. Reckert, and S. B. Kuzirian, dehydration and recovery of silica in analysis, 202
- Goulding, E., and O. D. Roberts, volatile oil from the leaves of *Barosma venusta*, 294
- Gourdon, M., the Southern Shetlands, 82
- Gowing-Scopes, L., symbolical representation of analytical operations, 247
- Gowland, W., "Metallurgy of Non-ferrous Metals" (review), 160
- Gray, A. W., "Production of Temperature Uniformity in an Electric Furnace" (review), 84
- F. W., and W. M. Birse, magnetic study of compounds of water and of aqueous solutions, 83
- Green, J. R., obituary, 288
- J. W., Institution of Chemical Technologists, 161
- Grey, E. C., volumetric determination of carbon in aliphatic substances in the wet way, 279
- Griffiths, E. H., and E. Griffiths, capacity for heat of metals at low temperatures, 33
- Grignard, O., and C. Courtot, derivatives of cyclopentadiene and its dimer, 107
- Günther, A. C. L. G., obituary, 288
- Guey, P. A., and F. E. E. Germann, gases retained by silver, 179
- HADFIELD, J. H., and J. Kenner, preparation of 3-nitro-otoluidine, 305
- Hadfield Research Prize, 234
- Haller, A., and R. Cornubert, syntheses by means of sodamide, 95, 107
- and J. Meyerh. (See Meyerh. ingh, J.)
- and M^{me}. Ramsart-Lucas. (See Ramsart-Lucas, M^{me}.)
- Hallimond, A. F., conduction of electricity at point contacts, 315
- Halogen hydrides, synthesis of optically active, 108
- Hamerton, Maj. A. E., Sir D. Bruce, Capt. D. P. Watson, and Lady Bruce. (See Bruce, Sir D.)
- Hammersten, O., "Text-book of Physiological Chemistry" (review), 282
- Harden, A., "Alcoholic Fermentation" (review), 119
- Hardman, R. T., R. Furness, and E. Newbery. (See Furness, R.)
- Hardness of solid solutions, 297
- Harper, E. M., and A. K. Macbeth, colorations produced by organic nitro-compounds with special reference to tetranitromethane, 315
- Hartung, E. J., new method for determining specific heats of liquids, 126
- Hayden, E. M., jun., and W. M. Thornton, jun. (See Thornton, W. M., jun.)
- Heart, antagonistic action of carbon dioxide and adrenalin on, 267
- Heilbron, I. M., A. A. Boon, and F. J. Wilson. (See Boon, A. A.)
- Helkesimastix facicola, living observations on the life-cycle of a new flagellate, 267
- Henderson, G. G., Society of Chemical Industry, 58
- and Maggie M. J. Sutherland, contributions to the chemistry of the terpenes, 70
- J. B., and L. A. Meston, freezing-point of milk, 259, 275, 283
- Hendrickson, A. V., "Gas Chemists' Summary, 1913" (review), 48
- Hermann, L., obituary, 289
- Hermann's phenomenon, 302
- Hewitt, J. T., Gladys R. Mann, and F. G. Pope, colour and constitution of azo compounds, 70
- Hexamethylenetetramine and phenol, anhydrous reaction between, 74
- Hill, G. W., obituary, 289
- Hinchley, J. W., "Chemical Engineering" (review), 257
- Hiorns, A. H., "Principles of Metallurgy" (review), 197
- Hodgson, T. K., and J. E. Purvis. (See Purvis, J. E.)
- Hollely, W. F., and R. Meldola. (See Meldola, R.)
- Holton, F. S., and W. L. Balls. (See Balls, W. L.)
- Homopiperonyl and homoveratryl alcohol, reaction of, 304
- Hönigschmid, O., revision of atomic weight of uranium, 162
- and M^{lle}. St.-Horovitz, atomic weight of lead from pitchblende, 128
- Hope, E., and R. Robinson, synthetic experiments in the group of the isoquinoline alkaloids, 279
- Hops, nitrogenous constituents of, 68
- Hostetter, J. C., method for determination of magnesium in calcium salts, 155
- Humfrey, J. C. W., part played by amorphous phase in the hardening of steels, 271
- Huntly, G. N., corrections in bomb calorimetry, 317
- Hutchinson, H. B., and K. MacLennan, determination of lime requirements of soil, 61
- Hutchison, C. G., and S. Smiles, interaction of nitric acid and the sulphides of *β*-naphthol, 83
- Hydrazoximes, isomeric, of camphorquinone, 69
- Hydrocarbons, calculation of constants for heats of combustion of, 73
- hydrogenation of cyclic, by sodium-ammonium, 48
- regularity between molecular heat of combustion and its bearing on constitution of, 26, 37
- Hydrogen and oxygen, catalytic action of copper oxide on combination of, 162
- lines, wave-lengths of, and determination of the series constant, 33
- potentials of acetic acid and standard acetate solutions, effect of dilution on, 292
- of mixtures of acetic acid and sodium acetate, 291
- Hydrogenation, catalytic, of liquids at moderate temperature and pressure, 12
- of compounds containing ethylenic bonds in presence of nickel, 174
- under ordinary pressure of aliphatic ethylenic compounds in presence of nickel, 193
- Hydrogenations by sodammonium, 162
- Hydroxides of lanthanum and the didymiums, action of bromine on, 49
- 4-Hydroxybenzylidenearylamines, polymorphic, produced by trituration and by influence of sunlight, 278
- Hydroxylamine derivatives of 1,4-diketones and N-oxy-2,5-dimethylpyrrol, 96
- CHLOPINE, W., and L. Tschugaeff. (See Tschugaeff, L.)
- Imperial College of Science and Technology, 134
- Indian plants, colouring matters contained as glucoside in flowers of, 69
- Indicator, methyl red as, 245
- preparation of dry starch for use as an, 195
- Indicators, some natural, 181
- Infinitesimal life of the, 23
- Institute of Chemistry, 72
- pass list, 60
- professional chemical qualification, 146
- Institution of Chemical Technologists, 161
- Ions, hemipermeability of the cellulose to, 81
- Ionisation, 244
- produced by gas reactions, 33
- Ireland, National University of, 145, 146
- Iriditrioxalates, optical decomposition, 185
- Iron and Steel Institute, 120
- Hadfield Research Prize, 234
- and aluminium, separation of zirconium from, with aid of ammonium salt of nitrosophenylhydroxylamine, 153
- and steel, determination of chromium and manganese in, 207
- corrosion and application to determine relative strengths of acids, 315
- production of high permeability in, 26
- separation of titanium from, with aid of ammonium salt of nitrosophenylhydroxylamine, 153
- Isocoumarin and isocarbostyryl derivatives, 280
- Isomerism, position, and optical activity, 267
- Isomorphism of perchlorates and permanganates, 246
- Isoquinoline alkaloids, synthetic experiments in the group of, 279
- Isothermal and adiabatic compressibilities of liquids between one and two atmospheres' pressure, 281
- JAEGER, F. M., "Isomorphism of the Ethylsulphates of the Metals of the Rare Earths, &c." (review), 132
- James, C., and D. W. Bissell, terbiun, 204
- Jamieson, G. S., and R. Wrenshall, determination of titanium as phosphate, 54
- J. S., notes on vinegar, 245
- Japanese varnish tree, death of, 68
- Jacques, A., "Complex Ions in Aqueous Solutions" (review), 208
- Jeans, J. H., potential of ellipsoidal bodies and the figures of equilibrium of rotating liquid masses, 32
- "Report on Radiation and the Quantum Theory" (review), 208
- Jenkin, W. M., method for the estimation of podophyllum resin, 206
- Jesson, E. M., and E. R. Bolton. (See Bolton, E. R.)
- Jevons, W., spectroscopic investigations in connection with the active modification of nitrogen, 286
- Johannia, J., catalytic action of copper oxide on combination of oxygen and hydrogen, 162
- oxidation and reduction of copper, 108
- Jones, B. M., dissociation of gaseous nitrogen trioxide, 279
- D. T., and R. V. Wheeler, composition of coal, 293
- H. C., E. J. Shaeffer, and M. G. Paulus. (See Shaeffer, E. J.)
- Marion, and A. Lapworth, *α*-bromonaphthalene, its physical properties and application to determination of water in moist alcohol, 70
- W. J., and J. R. Partington, ideal refractivities of gases, 70
- Joseph, A. F., note on a gas-pressure regulator, 305
- solutions of bromine in water, nitrobenzene, and carbon tetrachloride, 294
- Judd-Lewis, S., application of spectrography to analytical and industrial chemistry, 317
- Julian, Hester, "Memorials of Henry Forbes Julian" (review), 161
- Jungfleisch, E., and P. Landrieu, researches on the acid salts of dibasic acids, 12
- KALANDYKE, S. J., conductivity of salt vapours, ionisation produced by gas reactions, 33
- Kay, P., estimation of organic matter in water, 13
- simple methods for the determination of dissolved oxygen in waters, effluents, &c., 49
- Kaye, G. W. C., "X-Rays" (review), 36
- Keegan, P. Q., notes on plant chemistry, 211
- Keeney, R. M., and D. A. Lyon. (See Lyon, D. A.)
- Kelp as a source of potash salts, 232

- Kenner, J., reduction products of ethyl hydriodene-2:2-dicarboxylate, 293
and J. H. Hadfield. (See Hadfield, J. H.)
and Annie M. Mathews, di-phenyl-2:3:2':3' and 3:4:3':4'-tetracarboxylic acids, 293
Kenyon, J., investigations on dependence of rotatory power on chemical constitution, 280
and R. H. Pickard. (See Pickard, R. H.)
Kershaw, J. B. C., sources of the world's copper supplies in 1913, 258
Ketosisoketamines, 36, 173
Kew Observatory, atmospheric electricity observations, 35
King, H., possibility of a new instance of optical activity without an asymmetric carbon atom, 303
Kingscott, P. C. R., and R. S. G. Knight, "Methods of Quantitative Organic Analysis" (review), 257
Kling, A., M. Gelin, and M. Lassieur, researches on the alteration of milk containing bichromate, 48
Knight, R. S. G., and P. C. R. Kingscott. (See Kingscott, P. C. R.)
Knox, J., "Fixation of Atmospheric Nitrogen" (review), 59
Koehler, A., catalysis of butyric acid by thoria, 233
Koerner, G., asymmetrical 1.2 4-trinitrobenzene, 120
Kronecker, H., obituary, 289
Kubne, A., and E. Briner. (See Briner, E.)
Kunz, B., and M. O. Forster. (See Forster, M. O.)
Kuzirian, S. B., P. A. Gooch, and F. R. Reckert. (See Gooch, F. A.)
- L**ABORATORY reagents and glass apparatus, supply of, 174
Lactone, oxalocitric, and its transformation into tricarballic acid, 186
Lahay, M. J. M., effects of fatigue on blood pressure, 9
Lallemand, C., levelling of the earth, 31
Lamb, K. B., tests for determining quality of paper, 180
Lambert, B., and H. E. Cullis, wet oxidation of metals, 69
Lamble, A., and W. C. McCullagh, studies in catalysis, 267
Landrieu, P., and E. Jungfleisch. (See Jungfleisch, E.)
Lanthanum and the didymium, action of bromine on hydroxides of, 49
Lapage, G., and H. M. Woodcock. (See Woodcock, H. M.)
Lapworth, A., and Marian Jones. (See Jones, M.)
Lassieur, M., A. Kling, and M. Gelin. (See Kling, A.)
Le Bas, G., regularity between molecular heat of combustion and its bearing on the constitution of the hydrocarbons, 26, 37
Le Bon, G., evolution of matter, 31
Le Sueur, H. R., and J. C. Withers, mechanism of action of fused alkalis, 313
Lead, atomic weight, 8
corrosion, 69
from pitchblende, atomic weight, 128
obtained from different minerals, differences in atomic weight, 94
of radio-active origin, atomic weight, 128
oxyhalogenides of, 222
carbonate, nature of basic, 13
oxide, reduction, 173
- Lebeau, P., and M. Picon, hydrogenations by sodammonium, 162
of cyclic hydrocarbons by sodammonium, 48
Lee, R. E., J. F. Trickey, and W. H. Fegely, method for rapid quantitative analysis of bronze and brass, 183, 189
Leeds University, 138
Léger, E., transformation of barbaloin into β -barbaloin, 119
Lembert, M. E., and T. W. Richards. (See Richards, T. W.)
Lepape, A., and C. Moureu. (See Moureu, C.)
Lewkowitsch, J., "Chemical Technology and Analysis of Oils, Fats, and Waxes" (review), 281
Light, absorption by water changed by presence of strongly hydrated salts, as measured by the radio-micro-meter, 223, 235
quantitative measurements of, 255
Lime requirements of soil, determination, 61
Lime-water—calcium nitrate, three component system, 71
Linalol, constitution, 60
Lind, S. C., and C. F. Whittemore, radium: uranium ratio in carnotites, 218, 228, 239
Liquid masses, potential of ellipsoidal bodies and figures of equilibrium of rotating, 32
Liquids, adiabatic and isothermal compressibilities between one and two atmospheres' pressures, 281
catalytic hydrogenation of, 12
specific heats, new method for determining, 126
Literary announcements, 186
Lithium perchlorate, purity of fused, 39
Little, A. G., "Roger Bacon" (review), 84
Liverpool University, 139
Locquin, R., and P. Barbier. (See Barbier, P.)
London Chamber of Commerce, 234
City and Guilds of, Institute, 147
of, College, 147
University, 133
East London College, 8, 148
King's College, 134
University College, 134
Loring, F. H., mechanical liquid feeder, 199
melting-point of cane-sugar, 60
note on the question of associate atoms, 25
phosphorus and carbon, 210
Losanitch, M., fixation of sodium methylene compounds by ethylenic lactones, 96
Lowry, T. M., and V. Steele, a new chlorocamphor, 70
Lundell, G. E. F., and J. A. Bridgman, new method for determination of hydrocyanic acid and the alkali cyanides, 158
Lundie, M., is silica an indispensable constituent of plant food? 200
Lunge, G., "Technical Gas Analysis" (review), 305
Lyon, D. A., and R. M. Keeney, "Electric Furnaces for Making Iron and Steel" (review), 161
- MACBETH, A. K., and E. M. Harper. (See Harper, E. M.)
McCullagh, W. C., and A. Lambie. (See Lambie, A.)
Macdonald, J. S., man's mechanical efficiency, 10
- McIntosh, J., and P. Fildes, fixation of arsenic by the brain after intravenous injections of salvarsan, 266
McKenzie, K. J., A. A. Boon, and J. Trotter. (See Boon, A. A.)
MacLean, Ida S., and Sibyl T. Widdows, action of magnesium phenyl bromide on derivatives of phenyl ataryl ketone, 268
MacLennan, K., and H. B. Hutchinson. (See Hutchinson, H. B.)
McMaster, L. R., preparation and properties of the ammonium salts of organic acids, 212, 224
MacNab, W., "Lectures on Explosives" (review), 60
Madagascar, coal in, 24
Magnesium in calcium salts, determination of, 155
boride and amorphous boron, 293
phenyl bromide, action on derivatives of phenyl styryl ketone, 268
Magnetic field, photographic analysis of explosion flames traversing, 10
phenomena, the 27-day period in, 32
study of compounds of water and aqueous solutions, 83
Meilhe, A., and P. Sabatier. (See Sabatier, P.)
Mallock's observations on intermittent vision, note on, 31
Maltose, action of cold concentrated hydrochloric acid on, 269
velocity of hydrolysis of, by concentrated and fuming hydrochloric acid, 269
Man's mechanical efficiency, 10
Manchester, Municipal School of Technology, 143
Students' Roll of Honour, 221
University, 141
Manchot, W., compounds of nitric oxide with ferrous and cupric salts, 84
Mandel, J. A., "Text-book of Physiological Chemistry" (review), 282
Manganese, favourable action in acetic fermentation, 198
in iron and steel, determination, 207
sulphate hydrates, preparation, 107
thermo-chemical study of, 160
sulphide, estimation of manganese, 162
Mann, Gladys R., J. T. Hewitt, and F. G. Pope. (See Hewitt, J. T.)
Manuelli, C., solubility in water of nitrate compounds of calcium cyanamide, 84
Marangoni, A., and G. Scagliarini. (See Scagliarini, G.)
Marchant, Prof., investigations on the arc as a generator of high-frequency oscillations, 35
Marle, R. R., and D. R. Boyd. (See Boyd, D. R.)
Marqueyrol, M., and H. Murauer, action of acids on diphenyl-nitrosamine in hydroalcoholic solution, 48
Marshall, C. W., and J. A. N. Friend. (See Friend, J. A. N.)
Marston, E. C., the red thorn, 310
Masson, Flora, "Robert Boyle, a Biography" (review), 48
Mathews, Annie M., and J. Kenner. (See Kenner, J.)
Matricaria chamomilla, constituents of the flowers of, 291
Matter, evolution of, 31
Mayer, G., and A. Scheffer, chemical constitution of cellulose, 46
Meat preserved by cold, alteration of, 9
Meldola, R., and W. F. Holley, quinone-ammonium derivatives, 279
- Mellor, J. W., "Clay and Pottery Industries" (review), 163
Mercuric iodide, determination in tablets, 194
Mercury, atomic weight, 293
Merton, T. R., attempts to produce the rare gases by electric discharge, 31
Meserve, P. W., and A. Seidell. (See Seidell, A.)
Messel, R., Society of Chemical Industry, 55
Meston, L. A., and J. B. Henderson. (See Henderson, J. B.)
Meta-cresol, determining, volumetric method, 168, 176
Metals and alloys, thermal and electric conductivities of rarer, 35
capacity for heat at low temperatures, 33
wet oxidation of, 69
Metallography of German silver, 280
Metamethoxybenzaldehyde, 292
Methane and air, limits of inflammability of mixtures of, 294
propagation of flame in mixtures of, 294
velocities of flame in mixtures of, 267
oxygen, and nitrogen, propagation of flame in limit mixtures of, 294
Methoxy group, migration in decomposition of ammonium hydrate by Hofmann's method, 60
Methyl acetate, hydrolysis of, 267
Methylallylcyclohexanones, 119, 162
Methylbenzylcarbinol esters, optical rotatory powers of normal, 280
 β -Methylcyclopentanone derivatives, 95
Methylpropylcyclohexanones, 162
Methyl red as indicator, 245
sulphate and amine, interaction, 314
Meyer, A., azomethines derived from phenylloxazoline, 198
Meyeringh, J., and A. Haller, dimethylallylacetophenone and its oxidation products, 162
Micro-ammeter, photographic, 82
Mignone, G., and C. Moureu. (See Moureu, C.)
Milk containing bichromates, alteration of, 48
freezing-point of, 259, 275, 283
Minchin, G. M., obituary, 287
Mitchell, S. W., obituary, 289
Molybdates and tungstates, phenomena of transformation of, 174
of trivalent cerium, 174
Monaco, Prince of, marine animals of vertical migrations, 8
Monel metal, analysis of a sample, 196
 α -Monochloroketones, synthesis by zinc organo-metallic derivatives, 233
Montreal, International Exhibition, 1917, 84
Morgan, G. T., and J. H. Cooke, benzenesulphonyl derivatives of α -amino acids compounds, 303
and J. C. Elliott, p -chlorophenyl-selenious acid, 313
Morphine, characterisation by uranium salts, 233
Morrell, G. F., studies in the succinic acid series, 313
Morse, H. N., "Osmotic Pressure of Aqueous Solutions" (review), 161
Motor spirits, estimation of sulphur in, 163
Moureu, C., and A. Lepape, "Les Gases Rares des Grissous" (review), 119
and G. Mignone, diagnosis of primary, secondary, and tertiary bases, 96
ketosisoketamines, 36, 173
M., atomic weight of lead, 8

- Muller, J. A., heats of formation of hydrates of carbonylferrocyanides, 45
- Muraour, H., and M. Marquoyrol. (See Marquoyrol, M.)
- Murray, Sir J., obituary, 288
- Muscle, striated, vapour-pressure of contraction of, 9
- NAPHTHALENE** tetrahydride, preparation, 48
- β -naphthol sulphides and nitric acid, interaction, 83
- N*-Naphthyl-*n*-hexylcarbinol and its esters, rotatory powers of, 293
- National Relief Fund, 107, 186
- Canada's gift, 174
- Neale and Wilkinson, Ltd., presents and parcels for the troops, 173, 318
- Neogi, P., interaction of alkali alkyl sulphates and alkali nitrites, 267
- New South Wales, cyanogenetic plants of, 126
- Newbery, E., electro-motive forces in alcohol, 293
- overvoltage, 281
- R. Furness, and R. T. Hardman. (See Furness, R.)
- Newcastle-upon-Tyne, Armstrong College, 140
- Nickel, atomic weight, determination, 12
- bromination in presence of ethyl oxide, 162
- compounds of monovalent, 186
- steels, 24
- oxide, reduction, 173
- by hydrogen in presence of a dehydrating agent, 107
- Nickeling of aluminium, 198
- Nitrate compounds of calcium cyanamide, solubility in water, 84
- Nitric oxide, compounds with ferrous and cupric salts, 84
- gaseous, and chlorine, rate of combination, 83
- Nitrile, salicylic, 198
- Nitro compounds, colorations produced by organic, 315
- theories of formation of aliphatic, 267
- Nitrobenzene, solutions of bromine in, 294
- Nitrogen, liberation in reaction of NaOBr on urea, 117
- methane and oxygen, propagation of flame in limit mixtures of, 294
- sp.-spectroscopic investigations in connection with the active modification of, 286
- trioxide, dissociation of gaseous, 279
- 3-Nitro-*o*-toluidine, preparation, 305
- Nivière, J., determination of ethers in essential oils, 233
- Nolan, J. J., electrification of water by splashing and spraying, 32
- Northampton Polytechnic Institute, 148
- Norway, oil-hardening plant in, 214
- Nottingham, University College, 141
- N*-oxy-2,5-dimethylpyrrol, hydroxylamine derivatives of, 96
- Noyes, W. A., "Text-book of Chemistry" (review), 318
- Nuttall, W. H., and W. F. Cooper. (See Cooper, W. F.)
- Nyasaand, trypanosome causing disease in man in, 32
- OBITUARY.** Browne, Alfred John Juk, 288
- Burch, George James, 287
- Gaskell, Walter Holbrook, 288
- Obituary—
- Gill, Sir David, 287
- Green, Joseph Reynolds, 288
- Günther, Albert C. L. G., 288
- Hermann, Ludimar, 289
- Hill, George William, 289
- Kronecker, D. H., 289
- Minchin, George M., 287
- Mitchell, Silas Weir, 289
- Murray, Sir John, 288
- Poynting, John Henry, 287
- Riley, Dr. E., 185
- Ross-Clarke, Alexander, 288
- Smith Philip Henry P., 288
- Stratton, Lord, 288
- Suess, Edward, 289
- Swan, Sir Joseph Wilson, 287
- Weismann, August, 289
- Woodward, Horace Bolingbroke, 288
- Oceans and continents, primitive, 46
- Oddo, G., "Struttura Molecolare degli Atomii Radioattivi" (review), 11
- Oesch, J., and A. G. Perkin, alizarin α -methyl ether, 83
- colouring matters of Rhamnus catharticus, 281
- Oil fuel, water in, rapid methods of estimating, 245
- hardening plant in Norway, 214
- volatile, from leaves of *Barosma venusta*, 294
- Oils, essential, analysis, 120
- determination of ethers in, 233
- fish and marine animals as sources of, 198
- Oleaginous seeds and fruits, 317
- Olefine oxides, velocities of combination of sodium derivatives of phenols with, 69
- Olsen, J. C., "Van Nostrand's Chemical Annual, 1913" (review), 257
- and W. H. Ulrich, ozone in ventilation, 191
- Oones, K., a perpetual electric current, 23
- Optical activity and position-isomerism, 267
- of amino acids, influence of acids and alkalis on, 267
- of compounds without carbon, 210
- without an asymmetric carbon atom, possibility of a new instance, 303
- Optically active compounds, influence of solvents on rotation of, 281
- Orion nebula, 68
- Orthoaminoazo compounds, benzylphenyl derivatives of, 303
- Ortho-cresol, determining, volumetric method, 168 176
- Orthocyanophenol, nitro and amino derivatives, 198
- Orthonitrobenzylidenearylamines and their photoisomeric change, 70
- Ortho-vanillin derivatives, 280
- Oscillations, high-frequency, investigations on the arc as a generator of, 35
- Osmium-platinum, a new alloy, 62
- Ostwald, W., colloids, 43
- Overvoltage, 281
- Owen, D., bridge for the measurement of self-induction, 269
- F., and W. A. Bradbury. (See Bradbury, W. A.)
- Oxford University, 133
- Oxidations with bromine under influence of light, 174
- Oximes, isomerism of, 69, 292
- their sodium salts and methyl ethers, 69
- Oxygen and hydrogen, catalytic action of copper oxide on combination of, 162
- methane and nitrogen, propagation of flame in limit mixtures of, 294
- methods for determination of dissolved, in waters, effluents, &c., 49
- Oxyhalogenides of lead, 222
- Oxypropylene - dimethylacetophenone, action of epihalohydrins on, 12
- Ozonair, all about, 258
- Ozonation, air, 237, 252, 263
- Ozone in ventilation, 190
- PAPER**, tests for determining quality of, 180
- Parabenzquinone, reaction with sulphurous acid and with alkali, 292
- Para-cresol, determining, volumetric method, 168, 176
- Parker, A., and A. V. Rhead, velocities of flame in mixtures of methane and air, 267
- Parsons, C. L., radium, 284
- Parthenogenesis, stage of activation of phenomenon of, 23
- Partington, J. R., note on the dilution law, 304
- and W. J. Jones. (See Jones, W. J.)
- Pascal, P., relations between constitution and thermic properties of binary mixtures, 12
- uranyl sulphocyanide, 96
- Patent and Trade Marks Act of 1907, 161
- Patterson, S. W., antagonistic action of carbon dioxide and adrenalin on the heart, 267
- T. S., and E. F. Pollock, influence of solvents on the rotation of optically active compounds, 280
- Paulus, M. G., E. J. Shaeffer, and H. C. Jones. (See Shaeffer, E. J.)
- Peacock, D. H., preparation of phenylbenzyl ether, 302
- rotatory power and refractivity, 315
- Peddie, J. T., "British Industry and the War" (review), 252
- Penot's chlorometric method, 174
- β -Pentene and its derivatives, 96
- Pentene, preparation of normal, 12
- Perchlorates, isomorphism of, 246
- Perkin, A. G., carajura and chichard, 83
- note on quercitrin, 70
- and J. Oesch. (See Oesch, J.)
- and I. Shulman, colouring matters contained as glucoside in the flowers of some Indian plants, 69
- W. H. Jun., D. Bain, and R. Robinson. (See Bain, D.)
- and L. J. Goldworthy. (See Goldworthy, L. J.)
- W. M. Roberts, and R. Robinson, diketos-5,6-dimethoxy-hydridene, 281
- and R. Robinson, some derivatives of ortho-vanillin, 280
- Permanganates, isomorphism of, 246
- Perrier, E., death of the Japanese *W-rosh* tree, 63
- Petrie, J. M., cyanogenetic plants of New South Wales, 126
- Petroleum, water in, rapid methods of estimating, 245
- Petrols, origin of, 30
- Phalen, W. C., potash salts, summary for 1913, 219, 231, 241, 251, 261
- Pharmaceutical Society, 282
- School of Pharmacy of, 135
- Phenol and hexamethylene, anhydrous reaction between, 74
- determination in presence of hexamethylnetetramine and formaldehyde, 42
- determining, volumetric method, 165, 176
- resins in excess, 75
- Phenols, characterisation by uranium salts, 233
- Phenols, migration of para-halogen atoms in, 267
- sodium derivatives of, velocities of combination with olefine oxides, 61
- Phenyl benzyl ether, preparation, 302
- Phenylisoxazalone, azomethines derived from, 198
- Phenyl styryl *k*-tone derivatives, action of magnesium phenyl bromide on, 268
- Phisalix, Mde., antivenomous vaccinations, 67
- rabic virus and serpents, 47
- vaccination of rabies by venom, 30
- Phosphorus and carbon, 210
- Photogaphic micro-ampere-meter, 82
- Photokinetics of sodium hypochlorite solutions, 292
- Phototropy and thermotropy, studies in, 70, 278
- Physical Society, 33, 193, 244, 269, 315
- Physiology, foundation of new prize of, 23
- Pickard, R. H., and J. Kenyon, investigations on dependence of rotatory power on chemical constitution, 280, 293, 314
- Picon, M., preparation of normal pentene, 12
- and P. Lebeau. (See Lebeau, P.)
- Piergaolini, A., and R. Ciusa. (See Ciusa, R.)
- Piettre, M., alteration of meat preserved by cold, 9
- Pilcher, R. B., "History of the Institute of Chemistry of Great Britain and Ireland, 1877-1914" (review), 258
- Plant chemistry, notes on, 211
- food, is silica an indispensable constituent of, 200
- growth and nutrition, accessory factors in, 10
- Plants, cyanogenetic, of New South Wales, 126
- Indian, colouring matters contained as glucoside in flowers of, 69
- Platinum, preparing complex compounds of, 174
- Podophyllum resin, method for estimation, 206
- Pollock, E. F., and T. S. Patterson. (See Patterson, T. S.)
- Polytechnic, 147
- Pope, F. G., J. T. Hewitt, and Gladys R. Mann. (See Hewitt, J. T.)
- W. J., Address to Chemical Section of British Association, 103, 109
- Davy Medal, 291
- Potash, preparation from felspar and other sources, 175
- salts, summary for 1913, 219, 231, 241, 251, 261
- Potassium hydroxide, action of fused, on dihydroxystearic acid and dihydroxybenzoic acid, 33
- Potmesil, K., and E. Votocek. (See Votocek, E.)
- Poulton, Prof., Darwin Medal, 291
- Power, F. B., 234
- gold medal presented to, 270
- and H. Browning, jun., constituents of the flowers of *Anthemis nobilis*, 82
- constituents of the flowers of *Matricaria chamomilla*, 291
- Poynting, J. H., obituary, 287
- Pranke, E. J., present state of the cyanamide industry, 20, 28
- Procter, H. E., "The Making of Leather" (review), 131
- Propylcyclohexanones and methylpropylcyclohexanones, 162
- Propylenedimethylacetophenone oxide and some of its derivatives, 173

- Purvis, J. E., absorption spectra of the vapours and solutions of various derivatives of benzaldehyde, 292
and T. R. Hodgann, "Chemical Examination of Water, Sewage, Foods, and other Substances" (review), 306
Pyman, F. L., appointment, 234
a-Pyrone, preparation of derivatives of, from oxalacetic ether, 162
- QUEBRACHO** bark, alkaloids of, 313
Quercitin, 70
Quinone-ammonium derivatives, 279
- RABAUT, C.**, and J. Aloy (See Aloy, J.)
Rabic virus and serpe, ts, 47
Rabies, vaccination by venoms, 30
Radcliff, S., extraction of radium from Australian ores, 126
Radio-active substances, analysis by sublimation, 120
Radio-activity, acquired, 254
Radium, 264, 276, 284, 301, 310
emanation, action upon detonating gas, 210
in atmosphere, variation with altitude, &c., 234
essay competition on, 234
extraction from Australian ores, 126
uranium ratio in carnotites, 218, 228, 239
Raintall near Melbourne, influence of weather conditions upon amounts of nitric and nitrous acids in, 127
Ramart-Lucas, Mdme., and A. Haller, oxide of propylene-di-methylacetophenone and some of its derivatives, 173
synthesis by means of sodamide, 12
Ramsauer, C., analysis of radio-active substances by sublimation, 120
"Über die Analyse Radioaktiver Substanzen durch Sublimation" (review), 11
Ray, R. C., magnesium boride and amorphous boron, 293
Rays, ultra-violet, and serums, 31
new effects of, 8
Rayleigh, Lord, Rumford Medal 291
Raynaud, A., and F. Ducelliez. (See Ducelliez, F.)
L. Gay, and F. Ducelliez. (See Gay, L.)
Reading, University College, 143
Reagents, supply of, 174
Reckert, F. C., F. A. Gooch, and S. B. Kuzirian. (See Gooch, F. A.)
Redgrove, H. S., calculation of constants for the heats of combustion of hydrocarbons, 73
Redman, L. V., A. J. Weith, and F. P. Brock, determination of phenol in presence of hexamethylenetetramine and formaldehyde, 42
rapid volumetric method for determining o-, m-, and p-cresols, thymol, and phenol, 168, 176
synthetic resins, 64, 74, 118, 129, 149
Reddish School of Mines, 148
Refraction, atmospheric, and its bearing on transmission of electromagnetic waves round the earth's surface, 34
Refractivity, rotatory power and, 315
- Resins, synthetic, 64, 74, 118, 129, 149
Rhamnose, determination in presence of other methylpentoses, 198
Rhamnus catharticus, colouring matters of, 281
Rhead, A. V., and A. Parker. (See Parker, A.)
Rice, F. O., quantitative measurements of the absorption of light, 255
Richards, T. W., chemical significance of crystalline form, 50, 63
theory of compressible atoms, 22
and M. W. Cox, purity of fused lithium perchlorate, and its bearing upon atomic weight of silver, 39
and A. H. Fiske transition temperatures of the hydrates of sodium carbonate as fixed points in thermometry, 76
and M. E. Lembert, atomic weight of lead of radio active origin, 128
and J. W. Shipley, freezing-point of benzene as a fixed point in thermometry, 187
Richet, C., accustoming of ferments to toxic substances, 8
Richmond, H. D., "Daily Chemistry" (review), 246
Righi, A., "Ricerche Sperimentali sui Raggi Magnetici in Diversi Gas e Miscugli Gassosi" (review), 12
Rigoux, G., vision at a distance, 46
Riley, E., obituary, 185
River waters, the sulphate in, 307
Roal, H. E., vapour-pressure hypothesis of contraction of striated muscle, 9
Roberts, O. D., and E. Goulding. (See Goulding, E.)
W. M. W. H. Perkin jun., and R. Robinson. (See Perkin, W. H., jun.)
Robertson, I. W., G. A. Burrell, and F. M. Seibert. (See Burrell, G. A.)
P. W., and I. R. Gibbs. (See Gibbs, I. R.)
Robinson, Gertrude M., reaction of homopiperonyl and of homoveratryl alcohol, 304
R., D. Bain, and W. H. Perkin, jun. (See Bain, D.)
and R. P. Foulds. (See Foulds, R. P.)
and E. Hope. (See Hope, E.)
and W. H. Perkin, jun. (See Perkin, W. H., jun.)
W. H. Perkin, jun., and W. M. Roberts. (See Perkin, W. H., jun.)
Robyn, A., R. Fosse, and F. Francois. (See Fosse, R.)
Röntgen radiation, production of very soft, by impact of positive and slow cathode rays, 33
rays, chemical analysis by secondary, 8
Roscoe, Sir Henry, and Sir William Crookes as educationalists, 95
Society of Chemical Industry Medal, 58
Rosenhan, W., "Introduction to the Study of Physical Metallurgy" (review), 306
Rosenhaller, L., "Der Nachweis Organischer Verbindungen" (review), 84
Ross-Clarke, A., obituary, 288
Rotatory power and refractivity, 315
dependence on chemical constitution, 280, 293, 314
Roux, Dr., evolution of the spirilla of recurrent fever, 8
Royal Institution, 20, 233, 258, 302, 308
Society, 9, 31, 254, 266, 286, 302
- Royal Society, anniversary meeting, 287
Society of Arts, 258
Rubber, estimation of sulphur in, 317
- SABATIER, P.**, and L. Espil, reduction of oxides of copper, lead and nickel, 173
and A. Mailhe, catalytic decomposition of benzoic acid, 186
Safrole, derivatives, 267
St. Andrews University, 143, 145
St. Horovitz, Mle., and O. Höngschmid. (See Höngschmid, O.)
Salicylates, palladium, 198
Salt vapours, conductivity of, 33
Salta, acid, of dibasic acids, 12
ferrous and cupric compounds of nitric oxide with, 84
Salvarsan, fixation of arsenic by the brain after intravenous injections of, 266
Sandonnini, G., oxyhalogenides of lead, 222
Saponification of ether salts and amides by concentrated sulphuric acid, 27
Sazerac, R., and G. Bertrand. (See Bertrand, G.)
Scagliarini, G., and A. Marangoni, isomorphism of perchlorates and permaoganates, 246
Scheelite, rare earths in, 197
Scheffer, A., and G. Mayer. (See Mayer, G.)
Scheuer, O., action of radium emanation upon detonating gas, 210
reduction of carbon monoxide by hydrogen induced by radium emanation, 119
Schoeller, W. R., reduction of antimony and bismuth oxides by their sulphides, 317
Scientific appointments and salaries, 173
Scudder, H., "Electrical Conductivity and Ionisation Constants of Organic Compounds" (review), 305
Seeds, oleaginous, 317
Seibert, F. M., and G. A. Burrell. (See Burrell, G. A.)
and I. W. Robertson. (See Burrell, G. A.)
Seidell, A., and P. W. Meserve, determination of minute amounts of sulphur dioxide in air, 17
Selenium, influence of tellurium on sensitiveness of, to light, 162
Self-induction, bridge for measurement of, 269
Sénéchal, A., solid chromic sulphates, 186
Seuier, A., and Rosalind Clarke, studies in phototropy and thermotropy, 70
and R. B. Forster, studies in phototropy and thermotropy, 278
Sergeant and Folly, M.M., spirilla of recurrent fever, 23
Serpents, rabic virus and, 47
Serums and ultra-violet rays, 31
mechanism of inactivation of, 9
Shaeffer, E. J., M. G. Paulus, and H. C. Jones, absorption of light by water changed by presence of strongly hydrated salts, as measured by means of the radio-micrometer, 223, 235
Sheffield University, 142
scientific advisory committee, 254
Shelton, H. S., the sulphate in river waters, 307
- Shetlands, the Southern, 82
Shipley, J. W., and T. W. Richards. (See Richards, T. W.)
Shrewsbury, H. S., two rapid methods of estimating water in crude petroleum, oil fuel, and similar substances, 245
Shroder, J. H., and S. F. A. Lee, catalysis, 279
Shulman, I., and A. G. Perkin. (See Perkin, A. G.)
Sidersky, D., "Brennereifragen" (review), 48
Silica, dehydration and recovery in analysis, 202
is it an indispensable constituent of plant food? 200
Silicon, spectrum of elementary, 31, 113
Silver, atomic weight, 39
gas-a retained by, 179
German, metallography of, 280
Sir John Cass Technical Institute, 148
Sizings, rosin and glue, how to identify, 19
Slater, W. E., H. B. Dixon, and C. Campbell. (See Dixon, H. B.)
Smiles, S., and B. Ghose. (See Ghose, B.)
and C. G. Hutchison. (See Hutchison, C. G.)
Smith, H. G., and R. T. Baker. (See Baker, R. T.)
O. F., and J. R. Wright. (See Wright, J. R.)
P. H. F., obituary, 283
S. W., "Roberts-Austen, a Record of His Work" (review), 175
Smiells, C. J., and J. B. Cohen. (See Cohen, J. B.)
Snell, J. F., "Elementary Household Chemistry" (review), 197
Society of Chemical Industry, Annual General Meeting, 55
Liverpool Section, 258
London Section, 317
Nottingham Section, 257
of Public Analysts, 245, 317
Sodamide, action on 1,5-diketones, 96
synthesis by means of, 12, 95, 107
Sodammonium, hydrogenation of cyclic hydrocarbons by, 48
hydrogenations by, 162
Sodium amalgams, specific volumes and electrical conductivities, 293
derivatives of phenols, velocities of combination with olefine oxides, 69
acetate and acetic acid, hydrogen potentials of mixtures of, 297
carbonate hydrates, transition temperatures as fixed points in thermometry, 76
hypochlorite solutions, photo-kinetics of, 292
methylene compounds, fixation by ethyl-malic lactates, 96
molybdate and tungstate, phenomena of transformation, 120
Soil, determination of time requirements of, 61
Sollas, W. J., Royal Medal, 291
Solutions, hardness of solid, 297
Solvents, influence on rotation of optically active compounds, 220
Spectra, absorption, of oximes, their sodium salts and methyl ethers, 69
of sulphurous acid and sulphites, 35
of vapours and solutions of derivatives of benzaldehyde, 292
Spectral series, origin of, 286
Spectrography, application to analytical and industrial chemistry, 317

- Spectrum, band, of boron nitride 286
of elementary silicon, 31, 113
Spencer, L., photokinetics of sodium hypochlorite solutions, 292
Starch, action of cold concentrated hydrochloric acid on, 269
preparation of dry, for use as an indicator, 105
velocity of hydrolysis of, by cold concentrated and fuming hydrochloric acid, 269
Steel and iron, determination of chromium and manganese in, 207
Steels, part played by the amorphous phase in the hardening of, 271
Steele, V., and T. M. Lowry. (See Lowry, T. M.)
Strathcona and Mount Royal, Lord, obituary, 288
Strait, R. J., luminous vapours distilled from the arc, 254
Suess K., obituary, 289
Sugar, beet, capturing German trade, 209
cane, inversion by acids in water-alcohol solutions, 126
melting-point, 47, 60
Sugden, S., boiling-points in homologous series, 152, 165
Sulphate, chromic, solid, 166
in river waters, 307
Sulphites, absorption spectra of, 315
Sulphur in motor spirits, estimation, 163
in rubber, estimation, 317
phosphorescence of, 24, 60
dioxide in air, determination of minute amounts, 17
Sun is a star of the magnitude -26.5, 47
Sutherland, Maggie M. J., and G. G. Henderson. (See Henderson, G. G.)
Swan, Sir J. W. obituary, 287
Symbolical representation of analytical operations, 247
Syngamy in the trypanosomes, 267
Syntheses by means of sodamide, 12, 95, 107
Syphon, new form of intermittent, 163
- TABOURY, F.**, glucinum sulphate and its hydrates, 173
Takamine, J., enzymes of *Aspergillus niger* and the application of its amylolytic enzyme to the fermental industry, 215
Tannin, C., plurality of amyloses, 222
G., a new alkaloid, 31
constitution of galegine, 36
Tasmanian and Australian eucalypts, correlation between specific characters of, 126
Tassilly, E., and J. Canac. (See Canac, J.)
Taylor, E. K., capturing German trade, beet sugar, 209
H. S., and H. Bassett, jun. (See Bassett, H., jun.)
Telephone, thermophone, a new form of, 302
Tellurium, influence on sensitivity of selenium to light, 162
Terbium, 204
Terpenes, contributions to chemistry of, 71
Tetrahydro-2-naphthol and its esters, optical dispersive power of, 314
Tetranitromethane, co-operations produced by organic nitro-compounds, with special reference to, 315
- Thermometry, freezing-point of benzene as a fixed point in, 187
transition temperatures of hydrates of sodium carbonate as fixed points in, 76
Thermophone, new form of telephone, 302
Thermotropy and phototropy, studies in, 70, 278
Thomlinson, J. C., a useful laboratory vari-*ant*, 195
Thompson, F. C., metallography of German silver, 280
S. P., note on Mr. Mallock's observations on the intermittent vision, 31
"The Rose of the Winds" (review), 208
Thomson, Sir J. J., Copley Medal, 290
ionisation, 244
production of very soft Röntgen radiation by the impact of positive and slow cathode rays, 33
R. T., methyl red as indicator, 245
notes on bleached and unbleached flour, 245
Thoria, catalysis of butyric acid by, 233
Thoro, the red, 308
Thornton, W. M., jun., separation of titanium from iron, aluminium, and phosphoric acid with aid of nitrosophenylhydroxylamine (cupferron), 5
and E. M. Hayden, jun., separation of zirconium from iron and aluminium with aid of ammonium salt of nitrosophenylhydroxylamine, 153
Thujone and thujamenthene, 108
Thymol, determining, volumetric method, 168, 176
Tiffeneau, M., migration of a methoxy group in the decomposition of quaternary ammonium hydrate by Hofmann's method, 60
Tilden, Sir W. A., supply of chemicals to Britain and her dependencies, 295, 308
Time signals, registration of, 9
Tinckler, C. K., and F. Challenger, "Chemistry of Petroleum and its Substitutes" (review), 68
Tissot, M., mechanism of the inactivation of serums, 9
Tissues, validity of the microchemical test for the oxygen place in, 9
Titanium, determination as phosphate, 54
separation from iron, aluminium, and phosphoric acid with aid of ammonium salt of nitrosophenylhydroxylamine, 5
Toluenes, chlorination and bromination of substituted, 268
Townsend, J. S., Hughes Medal, 291
Tribenzoin, 132
Trickey, J. P., R. E. Lee, and W. H. Fegely. (See Lee, R. E.)
1,2,4-Trinitrobenzene, asymmetrical, 120
Triops, presents and parcels for, 173, 318
Trotter, L., A. A. Boon, and K. J. McKenzie. (See Boon, A. A.)
Trouton, F. T., address to Mathematical and Physical Science Section of the British Association, 91
Trypanosome causing disease in man in Nyasaland, 32
Trypanosomes, syngamy in the, 267
Tschugaeff, L., method of preparing complex compounds of divalent platinum, 174
and W. Ichon, compounds of monovalent nickel, 186
- Tschugaeff, L. A., chemical constitution of dioximes, 268
Tucker, A. E., Patent and Trade Marks Act of 1907, 161
Tungstates and molybdates, phenomena of transformation of, 174
Turner, W. E. S., displacing German trade, 258
Turpin, A., photographic micro-ampere-meter, 82
Tutin, F., and H. W. B. Clewer, constituents of *Clematis vitalba*, 82
Tyrer, D., adiabatic and isothermal compressibilities of liquids between one and two atmospheres' pressure, 281
- ULLMANN, F.**, "Enzyklopädie der Technischen Chemie" (review), 11, 95
Ulrich, W. H., and J. C. Olsen. (See Olsen, J. C.)
United States Geological Survey, 24
Uranium, atomic weight, 162
salts, characterisation of morphine and phenols by, 233
organic, 48
Uranyl glycolate and lactate, and some uranyl salts of polyacids of fatty series, 96
sulphocyanide, 96
Urea in blood, quantitative gravimetric analysis, 198
liberation of nitrogen in reaction of NaOBr on, 117
- VACCINATION** of rabies by venoms, 30
Vaccinations, antivenomous, 67
Van Risseghem, H., β -pentene and its derivatives, 95
Vanillinoxime, 292
Vanstone, E., sodium amalgams, specific volumes and electrical conductivities, 293
Vapour-pressures, new method for determination, 127
Vapours, luminous, distilled from the arc, 254
Varnish, a useful laboratory, 195
Ventilation, ozone in, 191
Veratraldoxime, 292
Vignolo, L., solvents of coal, 119
synthetic preparation of coal-gas, 198
Villiers, A., manganese sulphide, estimation of manganese, 162
Vinegar, 245
Vision at a distance, 46
intermittent, 31
Voelcker, J. A., "Royal Agricultural Society, Annual Report for 1913" (review), 222
"Woburn Experimental Station, Report on Field and Pot-culture Experiments, 1913" (review), 222
Volmar and Cousin, M. M. (See Cousin, M.)
Von Grawert, C. F., "Anorganische Peroxyde und Peroxide" (review), 11
Von Weimann, P. P., "Zur Lehre von den Zuständen der Materie" (review), 11
Von Weinberg, A., "Kinetisch-Stereochemie der Kinetisch-verbundenen" (review), 36
Votocek, E., and R. Potmesil, determination of rhombic in presence of other methyl pentoses, 198
- WALES**, University of, 135, 136
Walker, G. W., approximately permanent electronic orbits and the origin of spectral series, 286
Walpole, G. S., effect of dilution on the hydrogen potentials of acetic acid and standard acetate solutions, 292
Hermann's phenomenon, 302
hydrogen potentials of mixtures of acetic acid and sodium acetate, 291
Water analysis, hypothetical combinations in, 169
and aqueous solutions, magnetic study of compounds of, 83
electrification by splashing and spraying, 32
estimation of organic matter in, 13
in petroleum, oil fuel, and similar substances, rapid methods of estimating, 245
softeners, 318
solutions of bromine in, 294
Waters, effluents, &c., methods for determination of dissolved oxygen in, 49
fluorine in potable, 233
Water—calcium nitrate—lime, three component system, 71
Watson, Capt. D. P., Sir D. Bruce, Major A. E. Hamerton, and Lady Bruce. (See Bruce, Sir D.)
W. H., phosphorescence of sulphur, 60
and H. B. Baker. (See Baker, H. B.)
Weismann, August (obituary), 289
Weith, A. J., L. V. Redman, and F. P. Brock. (See Redman, L. V.)
Weizmann, C., and H. Bradbury. (See Bradbury, H.)
Wellcome Chemical Research Laboratories, 234
Werner, A., optical activity of compounds without carbon, 210
E. A., isomeric transformation of ammonium methylsulphate and of substituted ammonium methylsulphates, 314
simple demonstration of formation of biuret from interaction of carbamide and cyanic acid, 314
Wheeler, R. V., propagation of flame in mixtures of methane and air, 294
and M. J. Burgess. (See Burgess, M. J.)
and D. T. Jones. (See Jones, D. T.)
White, J., work of the public analyst in relation to manufactured products, 257
Whitmore, C. F., and S. C. Lind. (See Lind, S. C.)
Whitton, W. A., "First Book of Chemistry" (review), 185
Widdows, Sibil T., and Ida S. MacLean. (See MacLean, I. S.)
Williams, A., "Fire-damp Indicator or Methanometer" (review), 208
Wilson, E., additional note on the production of high permeability in iron, 286
F. J., A. A. Boon, and I. M. Heilbron. (See Boon, A. A.)
Withers, J. C., and H. R. Le Sueur. (See Le Sueur, H. R.)
Wohlgrumuth, H., researches on acyclic γ -halogeno acids, 60
syntheses of mixed organometallic derivatives of zinc, 162
Wolverhampton Municipal Science and Technical School, 148
Wood, F., "Sanitary Engineering" (review), 10

- | | | | |
|--|---|--|---|
| Wood, J. K., influence of acids and alkalis on the optical activity of some amino-acids, 267 | Woodward, Horace Bolingbroke (obituary), 283 | Wynne, W. P., 2:3-dibromonaphthalene, 71 | Zinc, organo-metallic derivatives, synthesis of aldehydes by, 233 |
| Woodcock, H. M., and G. Lapage, living observations on the life-cycle of a new flagellate, <i>Helkesimastix facicola</i> , 267 | Wrenshall, K., and G. S. Jamieson. (See Jamieson, G. S.) | | of α -monochloroketones by, 233 |
| Woodhouse, Hilda, and W. S. Denham. (See Denham, W. S.) | Wright, J. R., and O. F. Smith, variation of amount of radium emanation in atmosphere with altitude, &c., 234 | ZIMMERMANN, F., osmium-platinum, a new alloy, 62 | synthesis of mixed organo-metallic derivatives of, 162 |
| | R., absorption spectra of sulphurous acid and sulphites, 315 | Zinc, cadmium in, determination, 250 | Zirconium, separation from iron and aluminium with aid of ammonium salt of nitroso-phenylhydroxylamine, 153 |

END OF VOLUME CX

136138

P
Chem & Phys

Author Chemical News

Title

University of Toronto
Library

DO NOT
REMOVE
THE
CARD
FROM
THIS
POCKET

STORAGE

Acme Library Card Pocket
LOWE-MARTIN CO. LIMITED

